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THE
ANALYSIS
OF
INORGANIC BODIES.

BY

J. J. BERZELIUS.

TRANSLATED FROM THE FRENCH EDITION,

BY

G. O. REES.

LONDON:
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1833.

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TO THE

FRENCH EDITION.

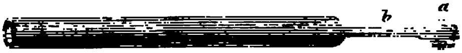
THE translation of this little work, which is inscribed at the end of the 12th volume of Berzelius's Elementary Chemistry, was made for a particular purpose. The translator has, however, been induced to publish it, both to gratify the desire of many of his acquaintance, and because he was himself convinced, that a treatise of this kind, short though it be, could not fail to be interesting, coming from a philosopher who has so much contributed to give perfection not only to analysis, but also to chemistry in general; for there are few branches of science that he has not elucidated by his researches, or extended by his labours. And though his countryman Scheel has rendered himself illustrious by showing what genius, combating against fate, could effect with small means, Berzelius has displayed in its full extent, the example of what genius can effect under favourable circumstances.

The notes which are added to this translation relate, for the most part, to subjects of which the author has spoken with great brevity; because he had treated of them more at length in the body of the work.

The general rules for ascertaining the different salts, that are placed at the end of the analysis, are extracted from the second volume of the Chemistry, as printed in the edition of 1826.

This addition was almost indispensable, because the author is exceedingly brief on this subject in the article on analysis; and he has himself stated that these rules are most important in analytical researches.

Fig. 1.



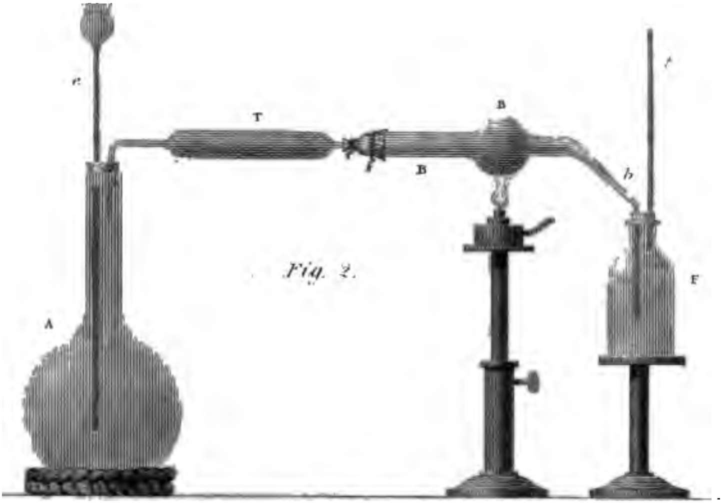


Fig. 2.

Henry Clark sc.

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DIRECTIONS
FOR THE
ANALYSIS
OF
INORGANIC BODIES.

In the class of inorganic bodies, I arrange all those that are not formed by animals and vegetables, and that do not result from their destruction by fire, putrefaction, or the action of acids, alkalies, &c. I comprehend under the term, the fossils, properly so called, the mineral waters, and the artificial products of bodies whose origin is not organic.—Chemical analysis tends at once to prove the knowledge, the judgment, and exactitude of the chemist. He must determine what those bodies are of which the substance he wishes to examine is composed, as well as the proportions in which they exist. Analysis is then of two kinds, qualitative and quantitative; and the former ought in every examination to precede the latter, since it is impossible to choose the best mode of ascertaining the proportions of the constituent principles of a compound before the nature of those principles is known.

The substances to be submitted to analytical research may present themselves under different forms; that is to say, they may be solid, liquid, or aeriform; and the analytical process will be different for each of these states of aggregation.

ON THE ANALYSIS OF SOLID BODIES.

The first thing to be done in the analysis of a solid body is to determine the quantity of water or volatile matters that it contains. The greater number of minerals contain a small quantity of water, foreign to their composition, which fills their interstices, and proceeds from the water which infiltrates into the interior of soils: it is for this reason that the fracture of a mineral is always found humid when it is first broken. Many crystallised minerals contain water of crystallisation; others, on the contrary, contain only interposed water, which produces the phenomenon of decrepitation when heated suddenly; lastly, some very porous earthy bodies, and some very soft minerals, often contain hygrometric moisture, which has been absorbed in the same manner that coal absorbs air and water. If the quantity of water is not ascertained, it disappears during the analysis, and a loss is sustained, for which no cause can be assigned.

A fossil may contain, besides water, other volatile bodies, generally carbonic acid, sometimes the hydrofluoric acid, or hydrochloric acid, and sometimes arsenious acid, or oxygen in excess; occasionally also it may oxidize more during the analysis. In all cases it is proper to calcine the mineral in a retort furnished with a tubular receiver, the bore of which receives a curved tube, which conducts the gas under receivers filled with mercury. To make these examinations, little porcelain retorts are generally employed, which can bear a high temperature. When none of this sort are to be had, little glass retorts, which may be self-blown with the least fusible glass, may be used: these little retorts can be employed when the examination is made at a moderate heat, such as that from the spirit lamp.

The retort is now balanced, and the substance for analysis is then placed in it, either entire or in powder, according to circumstances, and is weighed. In this way the loss is avoided, which would necessarily take place if the powder were weighed first and then placed in the retort. The neck of the retort is next adapted to the receiver, and a tube of caoutchouc is used for this purpose, without jointure, such as is obtained by cutting the necks of common caoutchouc bottles: it is by this means only that the presence of water proceeding from the corks or from the lute into the receiver can be avoided. The belly of the retort is placed in a little crucible, surrounded with sand, and heated by degrees to redness. When retorts of porcelain are used, they can be heated at once over the naked fire or in little draught furnaces. When the mass in the retort is in a state of ignition the heat may be lessened, if no gas disengages itself: in the contrary case, it is proper to continue to heat it as long as any thing is given off. The apparatus being cooled, a little water is generally found in the neck of the retort, which may be raised either with a piece of bibulous paper fixed to the end of an iron wire, or by heating the retort, and introducing a glass tube into the neck through which suction may be practised: in this manner the water soon evaporates. It is proper also to take this precaution before the experiment is begun, in order to be sure that the retort is perfectly dry. In deducting the new weights of the retort and its contents from the weights obtained before the calcination, the loss that the matter has sustained by the ignition is ascertained.

Many minerals, such as the augite, give forth some drops of an acid liquor which contains hydrofluoric acid: in this case there remains, after the evaporation of the water, a residue of silex upon the glass; and the liquor turns paper tinged by Brazil wood of a yellow colour. Sometimes the acid contained in the water is the fluoboric: in this case it does not affect the glass, and the Brazil-wood paper becomes first yellow, but acquires, after drying, a white colour in the place touched by the liquor. It is to be understood that if any other substance besides water distils, it is to be examined according to the rules that I shall establish.

After determining the water and other volatile bodies contained in a solid, the analysis is continued by dissolving this body. This is effected by either treating it immediately with an acid, or when that does not act, by calcining it with an alkali: by this calcination the combination at first insoluble is destroyed, and the property of being soluble in acids is acquired.

Hydrochloric acid is generally employed, or else a mixture of hydrochloric and nitric acids, the operation being carried on in a glass matrass by raising the temperature gradually to ebullition. The matrass is laid upon a sand bath, where it is inclined in such a way as to form an angle of somewhat less than 45° with the surface of the bath; in this way all the loss which might occur from effervescence or projection is avoided. The richer the glass is in silex and the poorer in oxide of lead, or, in other words, the more difficult it is of fusion, the better is it adapted for these experiments. It often happens that the glass becomes decomposed by the acids, while digesting the substances placed in it; and the best test that the glass can be submitted to, is to boil some sulphuric or concentrated nitric acid in it for some hours. If on washing the glass afterwards it is found to have lost its transparency, it may be concluded that it has been strongly attacked: if it be transparent whilst it is wet, but when it becomes dry looses its transparency at the place where it has been touched by the acid, it is less attacked than in the preceding case. Still, however, it ought not to be used in analysis. When there is no necessity to act on the mineral with aqua-regia it is best to form the solution in a platina crucible furnished with a cover having turned edges, taking care that the substances contained in the mineral cannot act on the crucible.*

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* When platina crucibles are used, M. Berzelius gives the following precautions: —

1st. Not to treat mixtures in them that can disengage chlorine.

2d. Not to fuse nitre, potassa, or soda (caustic) in them, as in this case there will be a formation of the protoxide of platina even without contact of the external air. This protoxide dissolves with a green colour in the alkali.

3d. Not to calcine mixtures in them that may leave a metallic residue; for example, the organico-metallic salts, nor mixtures that can give out phosphorus. In the former case an alloy forms, in the latter, a phosphuret; and in both cases the crucible will be attacked by the acids.

Aqua-regia should generally be employed when the substance for examination contains principles that for solution require in the first place to be oxidised. The substances that are not dissolved by repeated digestion in acids are silex, or portions of compound matter accidentally found in it.

The matter for analysis should be well pulverised: the complete decomposition often depends on this pulverisation. Very hard substances, such as minerals, are wrapped in paper, and broken on an anvil with a hammer: the

---

4th. When some metallic oxides are calcined, whose affinity for oxygen is less powerful, (oxides of lead, bismuth, copper, cobalt, nickel, antimony, &c.) care must be taken to raise the temperature to incipient whiteness; for although these oxides may be undecomposable of themselves, their reduction may nevertheless take place on account of the affinity which their metals possess for platina. It is true, that in heating the crucible, and treating it repeatedly with acid, the strange metals may be removed, but the internal parts of the vessel will in this way become porous, and it ought to be considered as spoiled.

5th. In strong and protracted calcinations it is proper to preserve the crucible as much as possible from the contact of coals, &c.: if this be not done, the platina combines under the united influence of coal and cinders with gradually increasing quantities of silex, and after some years' service it becomes brittle and cracked.

The fissures in platina crucibles can be filled with gold; but such crucibles do not bear so high a temperature as those which are perfect.

pieces so obtained are to be pulverised in calcedony or flint mortars, after which the powder is to be triturated on a slab of the same substance, and the fine powder is to be separated by decantation from those particles which are not as yet sufficiently triturated. A porphyry mortar may be used instead of calcedony; but this stone is less solid, and frequently allows particles to be rubbed from it into the powder. It is generally recommended to weigh the mineral before and after the pulverization, and to calculate from the augmentation of weight how much it has gained from the mortar; but this method, simple as it appears, is quite impracticable; for when trituration has been performed under water, in order to avoid the dispersion of the powder, the utmost difficulty is encountered when an attempt is made to remove and weigh it, so as to be able to draw any conclusion from it.

It would, perhaps, be easier to calculate the loss of the mortar by its weight before and after the pulverization; but the difference of weight obtained is seldom sufficiently great to render this precaution a real advantage.

The powder is heated to redness in a counterpoised platina crucible to drive off the hygrometric moisture, and to dissipate the dust which may have fallen from the clothes into the mixture during the long-continued pulverization. The powder is weighed in a glass capsule before it has time to acquire weight from the absorption of atmospherical humidity. It is to be remembered that in weighing any substance it should not be removed from a cold into a warmer room, for it will of course become heavier by absorbing water: these are trifles which we pass over, but which in an exact analysis deserve the greatest attention.

The compounds for examination result either from the combination of combustible or oxygenated bodies. I shall speak first of the latter class, since the combustibles should be oxygenated prior to being analysed. Substances soluble in acids are weighed in the vessels which are used for their solution; for it is hardly possible to remove a dry powder without its sustaining a greater or less loss: the acid is now added.

Some substances that before calcination were very soluble in acids lose this property by the process: we find it so, for example, with the bi and tri silicates of lime and alumina when hydrated. When bodies are acted on that possess these properties a portion is employed to determine the quantity of water present, and another to dissolve in acid and continue the ulterior analysis.

The calcination of bodies that are insoluble in acids is performed thus:—The powder being sufficiently triturated is placed in a platina crucible with carbonate of potassa reduced to a fine powder. To make the mixture a glass tube sealed at the extremity is used: the mixture being properly made, which requires much time, the tube is dried in a small portion of carbonate of potassa, which is afterwards to be thrown into the crucible.

The quantity of carbonate of potassa to be employed varies according to the nature of the substance: generally from three to five times the weight of the mineral may be used.

The crucible is covered and exposed to a gentle heat, which ought to be raised just to the fusion of the mass if it can be so managed: if it be heated too quickly, so that the fusion takes place suddenly, the ebullition produced by the disengagement of carbonic acid gas will project out some particles between the crucible and coverlid; then the process must begin again. A calcination kept up for one hour often suffices. Many minerals resist the action of carbonate of potassa, and can only be attacked by calcination with the alkali in the caustic state. All those that contain zirconia, columbic acid, or oxide of tin, are so circumstanced: they are the more difficult to be acted upon the greater the quantity of these substances which they contain. In these cases it is proper to use a silver crucible: the mineral powder, weighed, is first placed in it, then four or six times its weight of hydrate of potassa is added.

This operation requires a great deal of caution; for hydrate of potassa fuses easily, and the extrication of water causes a strong ebullition, by which a part of the fused mass may be cast out. It is then proper that the crucible should be covered with a lid that is hollowed out so as to give it a convex form.

The calcination proceeds best over a spirit lamp furnished with a circular wick, and a small iron plate chimney. By this arrangement an easily governed and sufficient heat is obtained; and there is no cause to fear that the crucible will be fused by too high a temperature. The ebullition having ceased, the heat is raised to redness, and is thus continued for at least an hour.

This calcination being finished, the crucible is left to cool, and the mass is then dissolved in diluted hydrochloric acid. The extraction of the mass from the crucible is easily performed: when carbonate of potassa is used there is no difficulty. The crucible is to be turned over a glass vessel of convenient size, and the mouth of the crucible is to be pressed lightly, so that the compression may not exceed the elasticity of the metal: the mass then detaches itself and falls into the glass: that which remains in the crucible is removed by means of diluted hydrochloric acid, and added to the saline mass which is in the glass vessel. Water is next thrown in; and the vessel is covered with a hollowed disc of glass having the form of a watch glass.

So much hydrochloric acid is added that no part of the mass remains undissolved; and when all effervescence has ceased it is to be heated gradually to drive off the carbonic acid entirely; for this gas will produce an ebullition by disengageing itself during the evaporation, which will occasion a loss.

When the decomposition is completed, the solution is transparent, and nothing remains undissolved, unless it be light flocculi resembling newly precipitated matter. If, on the contrary, part of the mineral has escaped decomposition it will remain at the bottom of the vessel, and when stirred with a glass rod it will communicate to the touch the same sensation as very fine sand: it is then necessary to recommence the operation with another portion of material. This generally happens when the substance has not been sufficiently triturated, as well as when in treating with water sufficient care has not been taken so that some of the less perfectly pulverised particles remain among the fine decanted powder.

When the calcination has been made with caustic potasssa the mass cannot be raised from the crucible. The external part of the crucible is then cleaned, and is placed in a porcelain capsule, so that those particles which are scattered by the effervescence collect in it. An excess of hydrochloric acid is added, so that the mass may be perfectly dissolved. The parts insoluble in the acid are generally portions of mineral unacted on. It is proper to submit these to a new calcination, so that no parts remain incapable of being attacked by the acids. With the crystallised minerals containing alumina, it often happens that after three or four calcinations insoluble matters still remain, which it is necessary to submit to a new calcination.

As the decomposition of these minerals presents so many difficulties, Chenevix has proposed to fuse them with from three to four times their weight of vitrified borax, which transforms them into a transparent glass at an incipient white heat. It is an advantage of this process that it may be executed in a platina crucible, and, consequently, at a very elevated temperature; but it has this great inconvenience, that when the mass is dissolved in hydrochloric acid the boracic acid remains, and does not dissolve so long as the supernatant liquor is acidulous. It happens that this mass requires a great quantity of water for its solution; and when the earths and metallic oxides have been precipitated, one cannot be sure that the precipitate does not contain boracic acid, which increases its weight. For these reasons I cannot recommend this mode of analysis in quantitative researches.

The mineral calcined with alkali having been totally dissolved in the hydrochloric acid, the complete separation of the constituents of the mineral is certain.

It remains then to examine, 1st, what are its constituents? 2d, in what proportions they exist?

QUALITATIVE ANALYSIS.

In this kind of analysis all the bodies whose presence is presumed in the mineral must be sought for, and it is necessary to prove that no others are present. For this purpose a determined quantity of the body must be employed for examination. It need not then be weighed with such great exactness. For the separation of silex the same process is used in qualitative and quantitative examinations. The hydrochloric solution is evaporated to dryness at a gentle heat: platina capsules are generally employed for this purpose; or if these be wanting, porcelain capsules; these last should be used only when the solution has been effected in nitro-muriatic acid; or when a body is present that can disengage chlorine, such as the oxides of manganese, cerium, &c. Glass should not be used, for the quality is never sufficiently good to resist the action towards the end of the evaporation. The capsule should be covered with paper, and the heat should never be so high as to make the liquor boil, for those portions thrown on the paper will be lost.

Towards the end of the process the mass which begins to solidify is to be stirred until it is perfectly dry, and until it no longer disengages the smell of hydrochloric acid: without this precaution the water will dissolve a portion of silex.

When the mass is perfectly dry, the peroxide of iron, the alumina, and magnesia, will have sometimes lost their acid, and will not be dissolved by the water.

The mass is then moistened with concentrated hydrochloric acid: the vessel is covered with a glass slab, and left to stand for some hours; it is then treated with water, and the solution is filtered: what remains on the filter is silica. When the calcination has been performed with caustic potassa, in a silver crucible, the silica thus obtained contains the chloride of silver; when the precipitate has been washed with distilled water, the chloride of silver is taken up by washing with caustic ammonia. The remainder is only silex, which is known by the following characters:—it is white, and ought to become more so by calcination, and to form a light earthy mass: it should not to be dissolvable by digestion in hydrochloric acid, and that fluid should not become coloured by it: fused on charcoal before the blow-pipe with an equal weight of soda, it ought to form a transparent colourless glass: on making it boil with a sufficient quantity of carbonate of soda, it ought to form (according to the experiment of M. Pfaff) a colourless and transparent liquor, which becomes gelatinous on cooling. Other indications than those we have just cited would announce the presence of strange matter; and it will in that case be proper to treat the silex, like the mineral powder, with a fresh quantity of potassa, in order to separate this strange body from it.

(B) The filtered liquid contains all the other substances in the form of chlorides: to investigate their nature we commence by adding caustic ammonia to the liquor until it possesses a slight ammoniacal odour. An excess of this alkali is necessary, for otherwise the precipitate will contain chlorides with an excess of base that often dissolve in the water when they are washed, and thus lead to error; but it is necessary to guard against adding too great an excess of ammonia, since it will dissolve a small portion of alumina. The ammonia precipitates all the bases less powerful than itself, and leaves in the liquor barytes, strontian, chalk, and magnesia*, and a portion of protoxide of manganese. If care has not been taken to make the iron pass into the state of peroxide, a portion of protoxide remains in solution. When the liquor contains zinc, nickel, copper, or cobalt, the greater portion of these oxides remain dissolved by the excess of ammonia.

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* Magnesia is precipitated by ammonia, except in an ascescent solution, when it is immediately re-dissolved by the ammoniacal salt formed. The solution is ascescent in the case here quoted, therefore the magnesia is left in the solution.

G. O. R.

(C) Ammonia, then, really precipitates the earths and metallic oxides. The liquor containing the precipitated matter is left to repose, that it may subside completely. It is proper to take the precaution of covering the vessel that contains it with a disc of ground glass so as completely to exclude the external air, since the carbonic acid may give place to a precipitate of carbonate of lime. The liquor is next filtered as quickly as possible, and the precipitate is washed, on the filter, with boiling water: when the filtration has commenced, this precaution ought not to be neglected until the precipitate becomes perfectly washed, if it be wished to avoid the presence of carbonate of lime.

(D) The filtered liquor is tested with sulphuretted hydrogen or sulphuret of potassium, to ascertain whether it contains a metallic oxide: if a precipitate be formed, it is examined before the blowpipe, which gives the best indications for detecting the inorganic bodies. I have spoken in my treatise on the Blow-pipe concerning the effects that each oxide produces, and I refer to that work, page 99. The presence of barytes or strontia in the liquid is ascertained by adding a few drops of a sulphate to it. Oxalate of ammonia precipitates the lime; and when that has been separated, phosphate of soda is added to the liquor to ascertain the presence of magnesia.

(E) The precipitate formed by the ammonia (C) is treated with a lixivium of caustic potassa, with which it is heated in a glass, silver, or platina vessel: the potassa dissolves the alumina and the glucina; filtration is performed, and the filtered alkaline liquor is saturated with hydrochloric acid; of which a sufficient quantity is added to dissolve the precipitated earths, after which an excess of carbonate of ammonia is thrown into the liquor. The alumina and glucina are precipitated; but the excess of carbonate of ammonia redissolves the latter: the liquor is filtered and boiled until it smells of ammonia: it becomes milky by the ebullition, and deposits the glucina, on ceasing to boil, in the form of a voluminous white powder. If a very great excess of carbonate of ammonia be added, a small portion of alumina will be dissolved, which often troubles the solution after a long boiling: it differs from glucina in its appearance; and on adding a small quantity of carbonate of ammonia to the precipitate the glucina dissolves in a few hours, whilst the alumina remains without alteration.

After having separated the alumina and glucina by the caustic potassa, the residue is treated with carbonate of ammonia, which dissolves the yttria, the zirconia, the protoxide and peroxide of cerium, and the peroxide of uranium: the solution of the three first is colourless, that of the two last is yellow. Those parts of the mass not soluble in ammonia are soluble in hydrochloric acid; if this acid, however, leaves a residue, this will be silica, colombic, or titanic acid, which may be decided by means of the blow-pipe.

Hydrochloric acid generally contains peroxide of iron and protoxide of manganese in solution: this is perfectly neutralised by caustic ammonia, or better still, such a quantity is added, that after a short maceration in the cold a precipitate of peroxide of iron is seen at the bottom of the vessel, so that the liquor still retains its yellow colour: then the remainder of the peroxide of iron is precipitated by a neutral succinate with an alkaline base; the oxide of manganese is next precipitated by boiling with carbonate of potassa. If the substance for examination contain alumina and magnesia, the precipitate of manganese contains also magnesia, which has been precipitated with the alumina by the ammonia (D). In this case the magnesia is separated from the oxides by means of hydrosulphuret of ammonia, which precipitates the protoxide of manganese of a pale brick colour: the colour will be darkened if the liquor still contains traces of iron, which frequently happens. The magnesia is next detected by the addition of phosphate of soda and caustic ammonia, when a double phosphate of ammonia and magnesia is precipitated.

(F) When the presence of an alkali is presumed in the matter for examination, it is proper, after having reduced it to powder, to mix it with five to six times its weight of carbonate of barytes, and to calcine it strongly for an hour or an hour and a half: the mass is next dissolved in hydrochloric acid; and after having separated the silica, as above mentioned, the barytes is precipitated by sulphuric acid. The other substances in solution are precipitated by carbonate of ammonia with an excess of base: the precipitates may be mixed, taken up, and washed on the same filter. The filtered liquor is evaporated; and when it has been reduced to a small bulk, a portion of oxalate of ammonia is added, to precipitate any of the lime which may yet exist in the liquor. The solution is next filtered and evaporated to dryness, and the saline mass heated to drive off all the ammoniacal salt present: if there be any residue, it is an acid sulphate with an alkaline base. I shall explain in quantitative analysis how the nature of the alkali in this salt may be known, and also how to distinguish the alkali from magnesia; for this last exists in the residue in the form of sulphate of magnesia, if the mineral examined contain that earth.

(G) Another and a shorter method is the following: — A mixture is made of one part by weight of the mineral, separated by water from the coarser parts, with two parts of fluor spar reduced to powder, and likewise treated with water to separate the coarser particles: the mixture being made, it is placed in a platina crucible; and after having added to it a sufficient quantity of sulphuric acid to transform the mass into a paste, it is heated gently. Fluo silicic acid disengages itself; and after having driven off the excess of sulphuric acid, the soluble salts can be separated by water from the sulphate of lime that is formed, and the alkali extracted by the rules given. When the presence of fluor spar is presumed, aqueous hydrofluoric acid previously prepared in platina vessels is used to act on the mineral: it is seen best whether a part of the mineral has escaped action by treating the mass evaporated to dryness with hydrochloric acid: the residue insoluble in this acid is taken up by the hydrofluoric acid. All having been dissolved, sulphuric acid is added, the solution is evaporated to dryness, and the mass calcined at a low red heat, in order to drive off all the hydrofluoric acid, which is especially necessary when the mineral contains lime. Analysis is facilitated by the habit of seeing and handling these matters; but it often happens that experienced chemists have confidence in the appearance of substances, and, consequently, they neglect experiments that would have changed their opinions. Hence it is that the youngest chemist often performs qualitative analysis exceedingly well, although, not being sufficiently acquainted with manipulation, he may fail in quantitative analysis; whilst the greatest masters are often deceived in qualitative decisions, either because they have too great a reliance in certain external signs, or because idleness increasing with years, they do not wish to make an examination, which cannot but confirm that which they know already.

I cannot then sufficiently recommend the prosecution of qualitative examination in its minutest details: not only does it give a great perfection to labour, but it procures occasionally the pleasure of discovering unknown bodies or combinations. The qualitative analysis of compound combustibles, such as the sulphurets and metallic arsenurets, &c. is best performed in the dry way by means of the blow-pipe. I refer for these examinations to the rules laid down in my treatise on the Blow-pipe.

If it be wished to perform this examination in the moist way, it is proper to treat these substances with aqua-regia, to transform them into salts; but this mode of operating is rendered exceedingly difficult by the property possessed by metallic acids of not being entirely separable from their combinations with different oxides by means of the alkalies; so that, without the use of the blow-pipe, very erroneous results will often be obtained.

Amongst the substances that present themselves for examination in an unburned state, there are some that form insoluble combinations with oxygen, or imperfectly soluble in aqua-regia. Sulphuret of lead, for instance, gives sulphate of lead; silver the chloride; tin leaves a deposit of oxide, which is insoluble when it is attacked by nitric acid only: in the same manner the molybdic and tungstic acids remain insoluble when the sulphurets of these metals are treated with aqua-regia. On adding water to concentrated acid solutions of antimony and bismuth, these oxides are precipitated, as is the case with many salts, such as the seleniates and sulphates of silver and of lead. Ammonia precipitates the greater portion of the metallic oxides, and holds in solution the oxides of silver, cobalt, copper, nickel, zinc, and cadmium, as well as the metallic acids. Carbonate of ammonia retains in solution all the oxides we have just named, except that of cadmium; it also dissolves the oxide of uranium, and the oxides of cerium. Caustic potassa dissolves the oxides of zinc, lead, tin, and the metallic acids.

The fixed carbonated alkalies dissolve a great number of metallic oxides, but in small quantities, so that this property is not available. Metallic iron precipitates arsenic, selenium, antimony, tin, bismuth, lead and copper, and those metals unalterable by the contact of air: it acts, but very slowly, upon the solutions of silver and mercury. Zinc precipitates all the preceding bodies, and cadmium also, which last is not precipitated by iron. Solutions containing titanium assume, after some time, a purple colour when treated with zinc in closed vessels, and solutions containing tungsten acquire a bright blue colour. Sulphuret of potassium precipitates from their solution in acids all the metals whose oxides in some way act as bases; but it dissolves all those oxides that act as acids; that is to say, those of selenium, arsenic, molybdenum, tungsten, antimony, tellurium, tin, gold, platina, and rhodium; nevertheless, it does not dissolve the green oxide of chromium and the titanic (peroxide of titanium), columbic, and silicic acids; it follows, therefore, that these compounds may be separated by sulphuret of potassium from the oxygenated combinations of other electro-negative metals.

Salts or saline fossils are often submitted to the examination of the chemist, and these require another process to discover the nature of the acid they contain. I shall state in a few words the method by which the inorganic acids may be known.

The sulphates with alkaline bases are reduced to the state of sulphurets, by heating them on charcoal with the blow-pipe.

In order to ascertain the presence of sulphur, Mr. Smithson recommends a drop of water to be placed on well polished silver, and the residue of the blow-pipe experiment to be put in contact with this water; after a short time the silver becomes of a blackish or brownish colour. When the sulphate has a metallic oxide for its base, it disengages sulphurous acid gas when exposed to the jet of the blow-pipe on charcoal; if the salt be soluble in hydrochloric acid, the sulphuric acid may be separated by means of chloride of barium; if on the contrary it be insoluble in water and acids, it is to be calcined to redness with an alkali; it is treated with water, the liquor saturated with hydrochloric acid, and then precipitated by a barytic salt: sulphate of barytes may be separated from the other barytic salts, difficult of solution, by means of acids that dissolve these latter salts without touching the sulphate.

The phosphates may be known by dissolving them in water or acids, and precipitating the phosphoric acid with acetate of lead; the phosphate of lead is not reduced by fusion on charcoal with the blow-pipe, and gives after cooling a bright grey bead, which at the moment of solidification assumes facets, owing to a commencement of crystallisation.

On fusing a phosphate before the blow-pipe with boracic acid and a small portion of iron filings, a bead of fused phosphate of iron is obtained.

The chlorides are easily known by the precipitates they form with the salts of silver and lead.

The fluorides are nearly all soluble in concentrated hydrochloric acid, and undecomposable by calcination with the alkalies; they disengage hydrofluoric acid when they are treated with concentrated sulphuric acid, and in this case the glass vessel is attacked. In order to make this examination, the salt and the sulphuric acid are mixed in a lead or platina vessel, covered with a glass slab, on which a coating of wax has been laid and partially removed by means of a pin: the hydrofluoric acid corrodes the glass in those places where the wax has been removed. If the matter examined contain only traces of hydrofluoric acid, the glass will not appear attacked after drying; but the attacked parts always appear when the glass is breathed on. When the matter for examination contains a mixture of a carbonate with a small portion of fluoride, the hydrofluoric acid is generally so quickly carried off by the carbonic acid disengaged with it, that it has no time to re-act on the glass; it is proper then to decompose or dissolve the carbonate before testing for the action of the hydrofluoric acid. The borates are known by treating them while hot with a powerful acid, they then become totally dissolved, but deposit the boracic acid on cooling in the form of scales; the mass mixed with alcohol, and inflamed, burns with a green flame, at least towards the end of the operation.

The arseniates may be known, because on heating them on charcoal with the blow-pipe they disengage an arsenical odour. Fossils often contain a mixture of arseniates and phosphates, which can be separated by precipitating the acids with acetate of lead; the arseniate of lead is easily reduced on the charcoal, whilst the phosphate fuses into a crystalline globule.

Chromic acid is known by its forming a soluble combination on calcination with potassa, which colours the water yellow; even when there is only a small portion of chromate of potassa present, the neutral liquor forms with protonitrate of mercury, a precipitate of the mercurial chromate, which gives by calcination a residue consisting of the green oxide of chromium. I refer for further particulars to my treatise on the blow-pipe, page 99. for the basis, and page 157. for the acids.

QUANTITATIVE ANALYSIS.

Of all the labours of the chemist, quantitative analysis presents most difficulties; it has reached a higher degree of perfection lately, owing to the doctrine of chemical proportions, either because analytical processes have been much improved by the researches, which it has been necessary to make in order to develope and confirm this doctrine, or that on comparing the results of analysis with the chemical proportions, the exactitude of the process may be tried. Thus the justice of an examination could not be proved but by repeating the analysis, so long as the absolute power of numbers did not contain theoretical interests of a higher class. This difficult proof was rarely employed, and the errors committed were doubtless rarely discovered, and analytical chemistry was as to the determination of proportions rather a faulty and difficult manipulation, than a true scientific research, leading to clear conceptions.

When chemical proportions and the laws concerning the affinities from which bodies combined by preference began to unfold themselves, chemical analysis became more valuable, and furnished a power of research and confirmation for the more elevated parts of theory. To arrive at just results it is proper to be well initiated in analytical manipulations, and this is not acquired but by much practice, which ought likewise to be accompanied with natural dexterity, without which no progress can be made in exact analysis. Persons who know a little chemistry ought to exercise themselves principally in quantitative analysis, persuaded that without being acquainted with its branches, they are quite incapable of all scientific research. It is necessary to be accustomed to weigh with the nicest exactitude, to pour out liquids without loss, so that the last drop does not run on the outer side of the vessel; it is necessary to keep an account of a variety of trifling things, the neglecting of which will render useless a troublesome process of many weeks. It is above all important to take care that no inattention, no unperceived circumstance destroy a process which approaches completion. Before this habit is acquired, the disappointment of losing an analysis is often experienced, through negligence or want of foresight; but this principle ought to be established, that an unsuccessful examination ought to be recommenced, and no corrections ought to be made, for however disagreeable it may be to recommence, it is still more painful to have performed a long and expensive process, without having a perfect conviction of the justice of the result, and that it may be valuable either to science or for the instruction of the person who has made the analysis. Since persons have commenced using the chemical equivalents to guide them in quantitative analysis, a great number of chemists have employed themselves in this mode of examination, and the less practised persons have drawn entirely false conclusions, from the confirmation they give to their results, by the agreement they present with the chemical equivalents, this agreement preventing them from suspecting their errors. It is then necessary not to trust too much to the result of an incomplete analysis, because it agrees with chemical proportions, and above all when several possible proportions approach to the numbers obtained, it requires extreme address and exactitude to determine which of these proportions is the true one. In analytical examinations a great many manipulations are requisite, which are best learned by seeing them performed, though many may be acquired by description.

The quantity of the substance for analysis depends on the sensibility of the balance; when the necessary address is acquired, a higher degree of exactitude is often obtained by operating on small than on large quantities; otherwise the quantity of re-agents employed, the time necessary for filtration, washing, and evaporation, augments of course the weight of the body.

Klaproth in his analysis generally used 100 grains; after his example I have used for some time the weight of five grammes*, corresponding nearly to the preceding weight; but experience has taught me that oftentimes this weight is too great. I prefer taking from one to two grammes, and I never use more than one grain when the mineral I wish to analyse contains alumina; for the precipitates of this earth are so voluminous, that when a larger proportion of the mineral is taken, it requires more than a week to wash the alumina. It is proper to add, that in cases where one of the constituents of a substance for analysis enters but in small quantity into the compound, its proportion should be determined by a particular analysis made on a larger quantity of material. I have already explained how silica is separated; in order to drive off all moisture, it is proper to calcine before weighing it, which process ought generally to be repeated on all inorganic substances that are not volatile. Calcination to incipient redness is performed in small platina crucibles, which have been previously weighed, and may be heated over a spirit lamp with a circular wick, and furnished with a small tin chimney. This calcination may be performed either by burning the filter, or by weighing it first with the mass, and next a portion of it before calcination; in the first case a paper is used that produces only a small quantity of cinder, and which gives, by often repeated experiments on larger portions of paper taken from different leaves, results proportional to the quantity of paper employed. The dried and weighed filter gives us, on calculation, following the preceding examination, a quantity of cinders proportional to its weight, which is to be deducted from that of the calcined residue. If, on the contrary, the weight of the filter be taken, according to the second method, before and after the desiccation of the precipitate, it is proper to put it in a crucible with a cover still warm, and when it cools, together with the crucible, it is to be weighed with it. If the operation be performed otherwise the weights will not be exact, for the paper always contains moisture when weighed in the open air. A portion of the dried mass is next weighed, with that portion of the filter that adheres to it, it is calcined, and that which the whole quantity contained on the filter has lost may be calculated by the loss of weight. I prefer the first process for silica, and in all cases where the calcined substance does not require any sort of process after the weighing.

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* A gramme is equal to nineteen grains; it is a French weight.

I choose the second method, however, when the weighed matter is to be submitted to other processes, in which cases the presence of bodies producing cinders might occasion error; this method is also employed whenever the reduction of a metallic body is to be feared.

In the case of silica it is proper to dry it completely before calcining it, to raise it from the filter with precaution, to place it in the crucible, and put the filter over it. If it be not perfectly dry, or if it cover the filter, a portion will be carried off by the gases disengaged during the calcination, for the silica obtained often appears in the form of an exceedingly fine and light powder.

After the separation of the silica, it remains for us to analyse the hydrochloric solution; but as the mode of proceeding is different according to the bodies it contains, and since it is impossible to give a formula applicable in all cases, I shall compensate for such an one by examples taken from real combinations, such as ordinary cases present.

First Example.—I proceed to describe the analysis of a mineral containing several substances, such as the orthite from the neighbourhood of Fahlun. We suppose that this mineral has been dissolved in aqua regia, the solution evaporated to dryness, and that the silica has been separated as above directed, so that the solution of the other substances in hydrochloric acid remains for analysis; we suppose it proved by a preceding trial that the mineral contains lime, alumina, yttria, peroxide of iron, protoxide of manganese, and protoxide of cerium.

(A) The water which was used to wash the silica having been reduced by evaporation to a very small bulk, is to be added to the acid solution, which is precipitated by an excess of caustic ammonia; the lime alone remains in the solution, which ought to be preserved from the contact of air, and left to repose, so that the precipitates may subside completely; the transparent fluid is next decanted, or, what is better, filtered, and the precipitate thrown on the filter. The funnel ought to be constantly covered by a disk of glass.

All the liquor being filtered, boiling water is at intervals thrown upon the precipitate, no fresh portion being added until the first has completely passed through; this is continued as long as a drop of the filtered liquor, on being placed on a platina spatula, leaves a mark after evaporation.

The washings are evaporated to a small bulk, afterwards they are added to the filtered liquid, which is precipitated by oxalate of ammonia, then it is heated gently, in order to make the calcareous precipitate subside; the oxalate of lime is filtered, washed, dried, and calcined with the filter. This calcination being intended not only to drive off the water, but also to transform the oxalate into carbonate, it is proper on heating it with the spirit lamp to cover the crucible three fourths, and to give it an oblique position. Along its inferior edge a thin band of iron is placed, which interrupts the current of heated air proceeding from the crucible, and favours the access of the atmospherical air: without this precaution, the mass often remains a whole hour without decomposition, although the crucible may be red hot, whilst by this, the oxalate is quickly transformed into carbonate; but as the heat may have driven off some of the carbonic acid, it is moistened with a concentrated solution of carbonate of ammonia, after which it is dried, calcined to incipient redness, and weighed; the weight of the lime is then calculated from the composition of the carbonate, which may be found in the tables exhibiting the atomic weights of inorganic bodies.

(B) The precipitate produced by the ammonia is composed of alumina, of yttria, of peroxide of iron, and the protoxides of manganese and cerium; these are to be digested at the temperature of 100° *, with a lixivium of caustic potassa, of which there may be a slight excess; those portions that cannot be raised from the filter may be removed by an acid and mixed with the rest. The potassa dissolves the alumina, and one may be sure that there is a sufficient quantity when the filtered liquor gives, on the addition of a drop of hydrochloric acid, a precipitate which redissolves immediately in the lixivium; when the contrary is the case, the precipitate ought to be digested with a fresh quantity of potassa. The alkaline liquor is next filtered, the insoluble precipitate washed, and the filtered liquor saturated with hydrochloric acid in excess, so as to dissolve the alumina, which is at first precipitated, after which, carbonate of ammonia is

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* 100° centigrade, equal to 212° of Fahrenheit.

added to the liquor in slight excess; the precipitate is to be well washed, dried, calcined, and weighed; it consists of alumina. To separate a small quantity of silica which it almost always contains, it is mixed with concentrated sulphuric acid, in a platina crucible, and heated gently. The earth swells, combines with the acid, and when the combination is complete, a sulphate of alumina is formed, which is to be dissolved in water; what remains is silica, which is collected on a filter and afterwards calcined and weighed. Its weight is deducted from that of the alumina.

Observation.—When the alumina constitutes the greater portion of the precipitate A, obtained by the ammonia, I am in the habit of drying, calcining, and weighing it, after which I dissolve it in hydrochloric acid, or in concentrated sulphuric acid. I next precipitate the other substances by an excess of caustic potassa. I filter, wash, dry, and weigh the precipitate, the weight lost is equal to that of the alumina. This process possesses the advantage of being quickly performed, since the separation of the alumina by caustic potassa is avoided, as also the washing of the alumina, which requires much time, in consequence of the great bulk of this earth when newly precipitated.

(C) The substances insoluble in the potassa are dissolved by hydrochloric acid; these consist of the protoxides of cerium and manganese, the peroxide of iron, and the yttria. In order to precipitate the protoxide of cerium, recourse is had to a peculiar process, founded on the property possessed by these oxides, of forming a double salt with potassa and sulphuric acid, which, though soluble in water, is insoluble in a saturated solution of sulphate of potassa, whether this solution contain free acid or not. A crust of crystallised sulphate of potassa is placed in the hydrochloric solution of these bases, which should rise above the solution, in order that every portion of the liquid may be saturated with this salt; the double sulphate of cerium and potassa precipitates, and when after four and twenty hours the solution takes up no more of the sulphate of potassa, the clear liquor is decanted, and the precipitate washed with an aqueous saturated solution of sulphate of potassa. The precipitate is next dissolved in boiling water, and caustic potassa is added to the solution (ammonia would precipitate a subsulphate)*, the precipitate is washed, dried, and calcined. In this manner the peroxide of cerium is always obtained, and if the mineral contains the protoxide, it must be estimated by calculation, and the surplus quantity of oxygen must be deducted.

(D) The liquor from which the oxide of cerium has been precipitated is saturated with ammonia, to separate the peroxide of iron from it by means of a succinate. This operation, to succeed, requires great care, since the least excess of acid has the effect of rendering the succinate of iron soluble, to a certain degree, so that it becomes gelatinous during the washing, and dissolves, giving a yellow colour to the liquid; the washings nevertheless deposit the succinate of iron, when they fall into a strong saline solution, which has been filtered before hand: this being the case, I have always employed with much success a concentrated solution of hydrochlorate of ammonia (muriate of ammonia) for the washing: after which I use a solution of caustic ammonia to deprive the precipitate of the sal ammoniac, by washing it with the caustic ammoniacal solution, but it is desirable to avoid as much as possible having recourse to these means.

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* An excess of potassa must be added, and left to digest, without which the precipitate contains a mixture of hydrate and subsulphate. In all cases the oxide must be dissolved after calcination, in order to be sure that it does not contain sulphuric acid.

To perform the precipitation well, you must commence by saturating the liquor with ammonia, of which a slight excess is added, so that a small portion of peroxide of iron is precipitated: when the ammonia is added it always happens that the oxide precipitates; but at the commencement of the operation, this oxide redissolves; after some time a small portion of ammonia is again added, the mixture is left to repose some hours at a temperature of 20° or 30° (centigrade; equal to 68° and 86° of Fahrenheit), and when the precipitate has disappeared, a few more drops of the ammonia are added, and the liquor again left to itself: this is to be repeated so long as any portion of peroxide of iron remains undissolved. The ammonia employed for this precipitation ought to be very weak: if the liquor lose all colour, it will indicate that all the iron has been precipitated, and that the excess of ammonia was too great. It is in this case proper to add more acid to the solution, and recommence the saturation with more care. When at length the point is attained, or a small portion only of iron is deposited, the precipitation is accomplished by a succinate, which ought to be perfectly neutral. The crystallised succinate of soda is most proper for this purpose. The succinate of ammonia is also used, but it is frequently acid, and that which is crystallised is always so; it is therefore proper to procure a solution of succinate of ammonia, which has neither an acid nor alkaline reaction: nevertheless, the succinate of ammonia is not used except in cases where the solution contains a fixed alkali, the weight of which it is wished to determine.

The succinate of iron precipitates of a pale red colour; the precipitation is completed on the application of heat, after which the precipitate is washed on the filter, and water charged with a small portion of caustic ammonia is thrown on it, in order to extract a part of the succinic acid. This precaution is taken in order to avoid the reduction of the iron to the state of protoxide, by too great a quantity of acid; it is of importance that the ammonia employed should be fresh and quite free from carbonic acid, for if that be not the case a small portion of succinate of iron will be dissolved.

The succinate of iron is to be calcined in a glass, or porcelain vessel, which ought at first to be covered, as the first impression of heat causes a slight decrepitation; but afterwards access of air may be allowed. The calcination may also be performed (with the before-mentioned precautions), in a platina crucible, placed obliquely: by not neglecting the precautions that I have just named, the red oxide of iron is obtained. It is true that some portions of the produce thus procured are attracted by the loadstone; but when the whole is digested with nitric acid, no considerable augmentation of weight takes place, so that this last treatment is useless. The succinates may be replaced by the benzoates for precipitating the peroxide of iron; these last salts, however, possess the disadvantage of affording a more voluminous precipitate, and of reducing a large portion of peroxide to the state of protoxide during the calcination, so that a mixture, in variable proportions, of per and protoxide is procured.*

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* By treating this mixture with nitric acid, it is easy to convert the whole into peroxide.

Mr. Herschel has proposed adding carbonate of ammonia, or ammonia nearly to saturation, to the solution containing iron; on boiling, the peroxide of iron precipitates in the form of a basic salt, whilst the manganese remains in solution as a double salt. If after being boiled the liquor still contains a small quantity of iron, a small portion of ammonia, or carbonate, is re-added, and it is boiled again.* When the liquor contains a fixed acid besides the peroxide of iron, such as the phosphoric, arsenic, boric, or hydrofluoric in combination with an earth, a compound which is precipitable by the alkali with the peroxide of iron (for instance when peroxide of iron and phosphate of lime are found dissolved together in an acid), Mr. Herschel's method is the best to separate the peroxide from the earthy salt; but it is to be remembered that the basic salt of iron which precipitates during ebullition contains a great part, and often the whole of the fixed acid, from which the peroxide of iron must next be separated.

If it be wished to precipitate the peroxide of iron only, without the phosphate of lime, there exists no way but by the addition of ferro prussiate of potassa to the acid solution, and washing the precipitate thus obtained (which treated with pure water frequently passes through the filter) with a solution of muriate of ammonia: the phosphate of lime is afterwards precipitated by caustic ammonia. In order to determine the quantity of the bodies which enter into any compound submitted to analysis, it is essential to know the degree of oxidation of the iron present, for which purpose we only possess means capable of approximation to the truth. For example, the sum of the constituent parts is too great when the iron is calculated as if found in the state of peroxide, or too small when it is supposed to exist in the form of protoxide; one generally supposes that the black or green colour of a mineral, indicates the presence of the protoxide, whilst the yellow or red colour, or absence of colour, is attributed to the combinations of the peroxide. All these indications are equivocal; for in the first place a mistake in analysis may render erroneous the calculation founded on a loss, or an excess; and again, the ferruginous coloured minerals often contain the protoxide and peroxide of iron, sometimes a combination of the two, in the proportion of one of protoxide to two of peroxide (oxidum ferroso ferricum), often in other proportions, and then the lime, magnesia, and the protoxide of manganese take the place of a portion of protoxide of iron, nearly in the proportions for forming the oxidum ferroso ferricum, so a great portion of protoxide is replaced by an equivalent proportion of another base; it is nevertheless probable, that the oxygen contained in the oxides of iron, constituting a mineral, may be determined by reducing it to a fine powder, and heating a given portion to redness, and making a stream of hydrogen, or sulphuretted hydrogen gas pass over it: the water may be received by chloride of calcium and weighed.

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* This process does not succeed well except when the iron is at the maximum of oxidation. Thus, it is proper to commence by boiling the liquor for some time with nitric acid, and to add ammonia or the carbonate while the liquor is still boiling.

Klaproth, to determine the quantity of peroxide of iron after calcination, mixes the mineral with oil, and heats it till carbonization is produced; by this mode he believes he always obtains the iron at the same degree of oxidation, which is erroneous, and in determining the quantity of iron, it should always be weighed in the state of peroxide to be sure of the result.

(E) The liquor from which the oxide of iron has been precipitated, still contains protoxide of manganese and yttria, which may be separated in two ways.

First Method. — The liquor is saturated with ammonia, the yttria precipitates, and the protoxide of manganese remains combined as a double salt, with a great quantity of hydrochlorate and sulphate of ammonia; — it is next precipitated with carbonate of potassa in excess, and the liquor is evaporated to dryness; the oxide of manganese then remains undissolved on the addition of water: after being washed and strongly calcined to redness, it may be estimated as a compound of 1 protoxide and 2 peroxide.

Second Method. — The yttria and oxide of manganese may be precipitated by carbonate of potassa, the liquor evaporated to dryness, and the precipitate washed with distilled water; the yttria is then dissolved in carbonate of ammonia. As it requires a great quantity of this last to perform the solution, this process is more expensive than the preceding. When the solution is boiled the ammonia disengages itself, and the yttria precipitates.

Second Example.—The presence of magnesia requires another form of examination; for alumina and magnesia have so great an affinity, that when a mixture of the two is decomposed by caustic ammonia, a part of the magnesia precipitates with the alumina in the form of aluminate of magnesia, if I may be allowed the expression. Alumina, which contains magnesia even in a proportion not exceeding 1 per cent, possesses after calcination the property of becoming exceedingly warm when moistened with water, which does not happen to pure alumina; if dried and calcined it again becomes warm on being moistened. If digested with concentrated hydrochloric acid it dissolves with difficulty, and leaves for residue a white insoluble powder. This is a combination of alumina and magnesia, analogous to that which is found naturally under the name of spinel. This powder can only be dissolved by ebullition. If before calcination the magnesiferous alumina is treated with caustic potassa it will not dissolve all the alumina, but the magnesia retains a certain portion by reason of its affinity.

(A) We will suppose a combination of silica, alumina, magnesia, lime, and of peroxide of iron, such as is presented in pyroxene or amphibole; we presume that the silica has been separated on the before-mentioned principles, so that the four following bases remain for separation, lime, magnesia, alumina, and peroxide of iron.

The acid liquor, from which the silica has been separated by filtration, is diluted with the washings, and poured into a cylindrical vessel, covered by a glass resembling a watch-glass in form. A solution of bicarbonate of potassa or ammonia is added to it by degrees; a strong effervescence is then produced, which might scatter a part of the liquor if the vessel were not covered during the addition of the bicarbonate. This salt precipitates the alumina and the peroxide of iron, but the lime and magnesia remain in the solution as bicarbonates. Let us first see to the treatment of the precipitate.

(B) The precipitate is well washed; but, when bicarbonate of potassa is used it is impossible to dry it in this state, and to calcine it to know the weight of the alumina by deducting that of the peroxide, since the alumina so precipitated contains carbonate of potassa in an insoluble combination; the precipitate is then removed from the filter (that part which remains attached to the paper being removed by an acid), and the mass is digested with caustic potassa, which does not dissolve the peroxide of iron; it is washed, dried, calcined, and weighed: if it should contain manganese it is to be redissolved in acid, and separated from it as we have directed in the preceding example. The alkaline liquor is saturated with hydrochloric acid in excess, so as to redissolve the alumina: it is next precipitated by carbonate of ammonia, and the precipitate washed with boiling water is dried and calcined; it should always be redissolved as above mentioned, in order to discover whether it contain silica.

Observation.—Many chemists are in the habit of precipitating the alumina from the alkaline solution, by hydrochlorate (muriate) of ammonia, in which case the hydrochloric acid saturates the potassa, and the alumina precipitates, whilst the ammonia is set free; but this last substance, especially when in great excess, dissolves a considerable quantity of alumina, which does not precipitate except on evaporation, so as to drive off all the ammonia; neglecting this, evaporation will necessarily cause a loss; besides, a circumstance presents itself in this case, to which sufficient attention is seldom paid, which is, that the great excess of caustic ammonia dissolved in the liquor favours the precipitation of part of the potassa with the alumina, so that when the analysis is carefully performed, an overplus is discovered when the constituents are summed up. If, on the contrary, the alumina is precipitated from its acid solution by carbonate of ammonia, the liquor contains free carbonic acid, which suspends entirely the affinity between the alumina and the alkali.

(C) The lime and magnesia are still to be separated, which two remain as bicarbonates in the solution from which the alumina and oxide of iron have been precipitated: there are many methods for effecting this separation.

First Method.—The solution is saturated by hydrochloric acid, the carbonic acid is driven off, and a slight excess of ammonia is added to the liquor; oxalate of ammonia is then added to it, so long as there is any precipitate, and the liquor is allowed to stand so that the separation may be complete; the precipitated oxalate of lime is filtered, and treated as directed in the first example, article (A).

The filtered liquor, added to the washings, is then evaporated, heated to ebullition in a glass matrass, and precipitated by carbonate of potassa; the clear liquor having been decanted, the precipitate is washed with a little water; the filtered liquor is evaporated to dryness, and the residue treated with boiling water, which leaves a fresh portion of magnesia undissolved. The liquor should have an alkaline re-action after the solution of the residue, otherwise another portion of alkali must be added, and the evaporation to dryness performed again: the two portions of magnesia are washed on the same filter with boiling water. These washings ought to be performed quickly, and should not be continued too long, since the magnesia is slightly soluble in them; according to Mr. Fife, 9000 parts of boiling water dissolve one of magnesia. If the washings are cold they filter more slowly, and one part requires only 2500 parts of water for solution. The magnesia is calcined and weighed in the caustic state, it is next dissolved in hydrochloric acid, the liquor evaporated to dryness, and redissolved in water containing a little hydrochloric acid. There always remains an observable quantity of silica: magnesia, protoxide of manganese, and oxide of zinc, retain it more than any other substances.

Second Method.—The liquor is saturated with carbonate of potassa and evaporated to dryness, the saline mass is treated with water, which dissolves neither the carbonate of lime nor magnesia, and when it is well washed it is saturated with pure sulphuric acid, and heated to incipient redness.

The mass is weighed, afterwards it is treated with a saturated solution of sulphate of lime, which only dissolves the sulphate of magnesia: what remains is the sulphate of lime, which is calcined and weighed, and by deducting its weight from that of the two sulphates, the weight of the sulphate of magnesia is ascertained. The quantity of the two bases is calculated from the composition of their sulphates found in the atomic tables.

Third. The lime is precipitated, as before, by oxalate of ammonia; a solution of phosphate of soda, containing a little ammonia, is added to the remaining liquor, which contains hydrochlorate of magnesia (for the simple neutral salt is not precipitated); the precipitate is the ammoniaco-magnesian subphosphate: it is washed, calcined, and weighed. This method, which has been proposed lately, is not perfectly exact; for the precipitate, although insoluble when the liquor contains an excess of phosphate, is dissolved on the addition of pure water, and precipitated anew from this solution when a phosphate is added. This solubility, which has not been taken into consideration, renders the result equivocal. This error, nevertheless, has been corrected by another error, viz. the supposition that the calcined precipitate contains 40 per cent. of magnesia, whilst it contains but 36.67: it follows that that which has been lost by the washings, has been replaced by the supposition of a greater quantity of magnesia. However this may be, it appears that it is preferable to precipitate the magnesia with carbonate of potassa, in the way we have before mentioned; or to evaporate the liquor to dryness, and calcine the salt:

on treating it with water the magnesia remains untouched.

Observation.—In those cases where the earths contain protoxide of manganese also, this last must be first precipitated by hydrosulphate* of ammonia, the precipitate washed and dissolved in hydrochloric acid; the solution is then mixed with carbonate of potassa, and evaporated to dryness; the dried mass is digested in water, which does not take up the carbonate of manganese: it is washed on a filter, dried, and calcined. If the quantity be great, it is necessary to be sure that it does not contain silica, as I have said concerning magnesia.

Manganese can also be precipitated by ferrocyanuret of potassium; a reddish white precipitate forms, which, to be washed without passing through the filter, requires the same precaution as the prussian blue; that is to say, a solution of sal ammoniac must be used as a lavement: the precipitate of the ferro-cyanuret of manganese is calcined, the iron is calculated as being in the state of protoxide, and the manganese as peroxide.

Third Example. When minerals contain an alkali, recourse must be had to a particular process in order to extract it; which is easily effected when the mineral is soluble in an acid. If it contain, for instance, silica, soda, lime, and alumina, such as the mesolithe, the pulverized mineral is dissolved in hydrochloric acid: the solution genenerally becomes gelatinous, and is to be evaporated to dryness; it is then moistened, first with hydrochloric acid, and then with water; after which the silica is separated by filtration and washed. Ammonia is added to the solution, which precipitates the alumina, and, lastly, the lime is separated from the filtered solution by the oxalate of ammonia; the liquor then contains nothing more than the fixed alkali, except sal ammoniac: it is evaporated to dryness, and the salt heated in a balanced platina crucible, until no more sal ammoniac is given off; after which the residue is weighed. This should not be heated to fusion, for at that heat a part of the alkaline chloride might volatilise: this chloride has potassa, soda, or lithia as base; the last is deliquescent, the two former are not so. If after the addition of oxalate of ammonia the solution be not heated, the whole of the lime will not be precipitated; and thus the residue will contain chloride of calcium, which attracts moisture: but its presence is easily ascertained, as the solution precipitates with carbonate of ammonia. If the mineral contain magnesia, this will remain in the calcined mixture, and may be easily separated by water, which does not dissolve it, so that its weight may be determined.

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* Hydrosulphuret of ammonia.

There are many means of determining whether the alkali present be potassa or soda: tartaric acid, for instance, may be added to the saline solution, and evaporated gently,—an acid tartrate of potassa then precipitates; or else a solution of fluoric acid may be added, which precipitates the fluosilicate of potassa. It may likewise be tested with a solution of chloride of platinum; in this case a double salt of potassa and platinum precipitates: if none of these indications are exhibited, soda is the base of the salt present.

If by chance a mixture of the two alkalies presents itself, it is rather difficult to separate them so as to determine their proportions exactly. Of many methods which I have tried the following has succeeded the best: the salt obtained is mixed with 3¾ its weight of the crystallised double chloride of sodium and platinum; this proportion is just sufficient for the potassium to replace the sodium contained in the double salt, should the salt examined contain only the chloride of potassium. The mixture is dissolved in a small quantity of water, evaporated to dryness by a gentle heat, and then treated with alcohol. This menstruum dissolves the chloride of sodium contained in the mixture, as well as the excess of the double chloride of sodium and platina, but does not act on the double salt of potassium and platina which is formed. It is washed with alcohol, dried, and weighed: 100 parts of this salt contain 30.73 of chloride of potassium. By deducting its weight from that of the saline mixture employed, the quantity of chloride of sodium is ascertained: the quantity of the alkali is calculated from the weight of the chloride.

Observation. — The chloride of platinum alone cannot be easily employed; for a slight excess of this salt renders a small portion of the potash salt soluble in alcohol; which, besides, has a great tendency to decompose the simple salt of platinum. Moreover, the double salt is so soluble in water that it is absolutely necessary to use alcohol.

Fourth Example. When a mineral containing alkali is insoluble in acids, it must be reduced to a fine powder, and the coarser parts separated by water, as we have above directed; then, after having dried the powder again, it is calcined with five times its weight of carbonate of barytes, obtained by precipitating the uncrystallised nitrate of barytes by carbonate of ammonia. The calcination is to be performed in a platina crucible, at a very high temperature; a semifused mass is obtained, which is dissolved in very weak hydrochloric acid: the silica generally remains, in the state of an insoluble flocculent powder. The solution is evaporated to dryness, and is treated as before directed to separate the silica. If it be wished to determine not only the quantity of potassa, but also that of the other ingredients, these latter are precipitated by ammonia, and the remainder of the process is continued as above described; after which the barytes is precipitated by sulphuric acid: but it is better to determine the quantity of the other bodies by treatment with an alkali; and the quantity of the alkali contained in the mineral by a separate process, by means of carbonate of barytes. For this purpose, after having separated the silica, a mixture of sulphate of ammonia and caustic ammonia is added to the liquor; the alumina, the oxide of iron, and sulphate of barytes precipitate together: their precipitate is much less voluminous, and consequently easier to wash, than that of the alumina alone would have been. (An analysis of the precipitate may now be made, by treating it with hydrochloric acid, which dissolves every thing except the sulphate of barytes.) As the filtered solution may contain lime, it must be treated with oxalate of ammonia, filtered and washed. The clear liquor is added to the washings, evaporated to dryness, placed in a balanced platina crucible, furnished with a cover curved inwards. It is heated with great care; the mass decomposes with a slight ebullition, ammonia and sulphate of ammonia disengage themselves, and there remains a liquid mixture, consisting of an alkaline supersulphate, which is capable of supporting a prolonged heat before it becomes neuter. In order to drive off the last excess of sulphuric acid, I am accustomed to place in the crucible, by means of a platina spoon, a piece of carbonate of ammonia, which I cover directly with the lid; leaving the spoon in till all the carbonate of ammonia is evaporated. The carbonate of ammonia can only be placed in the crucible when the mass is perfectly solid, otherwise the liquid salt boils and splashes the spoon; it is afterwards exceedingly difficult to determine the weight of the salt attached to the spoon. In this way the excess of sulphuric acid disengages itself, unites to the ammonia, and the alkaline salt becomes neuter. In order to ascertain what the alkali united to the sulphuric acid may be, the salt is dissolved and crystallised; the sulphate of potassa is then easily distinguished from the sulphate of soda or of lithia, when these salts alone are present: but when there is a mixture of these sulphates, or the form of the crystals obtained is not well determined, a known quantity of the calcined salt must be taken and dissolved in water, and acetate of baryta added; the filtered liquor is evaporated to dryness, and the acetate transformed into a carbonate by calcination. By treating the residue of the calcination with water, the baryta which has been added in excess remains in the state of insoluble carbonate; the solution is next saturated by hydrochloric acid, and evaporated to dryness. If the salt so obtained be deliquescent it is the chloride of lithium; if it be not so, it must be treated as we have before mentioned with the double salt of platina. — (Vide example 3.)

When the mineral contains magnesia, this is obtained together with the alkaline sulphate in the form of sulphate of magnesia; its presence is detected by making a concentrated solution of the saline mixture, and by adding to it a great excess of caustic ammonia, which precipitates part of the magnesia: if this happen, the mixture is evaporated to dryness, to drive off the ammonia; it is re-dissolved in water, and treated with acetate of baryta, as we have before said. After calcination the magnesia remains insoluble, so that the alkali can be separated by water.

Observation. — Nitrate of barytes was formerly used to decompose minerals containing an alkali: this custom is discontinued, because the nitrate oxidizes the platina crucibles, and consequently cannot be employed except when operating with silver crucibles, which are themselves slightly attacked, so that chloride of silver is obtained with the silica; besides, the nitrate of barytes fuses and boils up, so that during the calcination losses are sustained from the splashing. Gehlen first proposed the employment of carbonate of barytes; more lately Eggertz has tried the employment of oxide of lead in the analysis of the albite; and M. Berthier not long since proposed the nitrate of lead for platina crucibles, and the oxide of lead for clay crucibles, in making the analysis of all minerals containing alkali. Although the oxide of lead may be used from necessity, it nevertheless presents many inconveniences, the principal of which consists in the danger incurred by the crucibles should the lead be reduced, for they will be destroyed; besides, it dissolves easily in hydrochloric acid. The nitric acid must, therefore, be employed for the solution of the calcined mass then, after the precipitation of all the dissolved substances by ammonia, a large quantity of nitrate of ammonia is obtained, which swells and splashes during evaporation to dryness: finally, an alkaline nitrate is procured, from which the weight of the alkali cannot be calculated with such nicety as from the sulphate or chloride. In a quantitative analysis exact results are of such importance, compared with the pecuniary value of the tests, that there is no economy in neglecting to use the best re-agents that can be procured. The weight of the alkali may also be determined by using hydrofluoric acid as above mentioned, or a mixture of pure fluor spar and sulphuric acid (*qualitative analysis*, G), so as to render soluble the constituents of the insoluble mineral; the sulphate obtained is then examined according to the preceding rule.

Fifth Example. We have now to examine combustible bodies; for instance, a combination of the sulphurets of copper, iron, and zinc.

(A) The compound is pulverised, and treated with aqua regia in a glass matrass; the metals dissolve, leaving the sulphur; the digestion is continued until the sulphur remains in the form of little drops. To accelerate the analysis, these may be separated by filtration, washed with care, so that they may contain nothing of the solution; then dried by a gentle heat, and weighed. Part of the sulphur passes to the state of sulphuric acid; therefore chloride of barium is added to the liquor, the precipitate of sulphate is dried and calcined, and gives the quantity of sulphur by calculation according to the atomic tables. The excess of barytes is next precipitated by sulphuric acid; or, which is better, another portion of the mixture for examination is dissolved, to determine the proportion of metals. The liquor should be strongly acid; a stream of sulphuretted hydrogen is passed through it, which gives a precipitate of bi-sulphuret of copper; it is dissolved in nitric acid, the sulphur separated from it by filtration, and the copper precipitated by an excess of caustic potassa: or the excess of acid is driven off by evaporation, and just a sufficient quantity of ammonia is added to the liquor to redissolve the oxide of copper; after which a solution of caustic potassa is added to it, until all the oxide of copper is precipitated, and the liquor has lost its colour. This result is more easily obtained when the solution is concentrated; when it is weak, it requires some hours completely to precipitate the oxide of copper, which is in the state of blue hydrate. When ammonia has not been added, the precipitate is gelatinous, and difficult to wash; whilst the presence of this alkali renders it granular, heavy, and easy to wash. The filtration is performed on a weighed filter, and the washing with boiling water; it is next dried and calcined without the filter:

the weight of the deutoxide of copper gives that of the metal.

(B) The remaining liquor is mixed with nitric acid, and brought to a state of ebullition, either to oxidise the iron, or to drive off the excess of sulphuretted hydrogen; it is next left to repose, and the sulphur which precipitates is separated by filtration and washing. The transparent liquor is saturated with ammonia, so as to precipitate part of the oxide of iron; after which the whole of the iron is precipitated by the succinate of soda, as above mentioned (Ex. 1st, D,) the solution is filtered, the precipitate washed, and the zinc precipitated by carbonate of potassa; the whole is evaporated to dryness: all the ammonia being driven off, the mass should be alkaline, if all the zinc has been precipitated. The mass is now treated with water, which dissolves the alkaline salt, and does not act on the oxide of zinc: this last is washed, dried, and calcined. It gives the weight of the zinc, which, added to the weight of the sulphur, of the copper, and of the iron, ought to give a total equivalent to the weight of the mixture employed.

Observation.— Klaproth is accustomed to precipitate the copper by iron; the copper so obtained is washed, dried, and weighed: but only an approximation to the truth is obtained by these means, either because the copper absorbs oxygen whilst drying, or because portions of iron, precipitating frequently, mix themselves with the copper, resembling soot in appearance: it is then impossible to determine the exact weight of it. This method is, however, very good when performed in the following manner:— Sulphuric acid is added to the solution of copper, which, when it contains nitric acid, is evaporated until this last acid is entirely driven off; it is next diluted with water, and boiled. As soon as the liquor boils a well polished plate of iron is placed in it, or, what is better, a large band of iron plate, cleaned with weak sulphuric acid, and the digestion is continued until all the copper is precipitated. The copper is next separated from the iron, washed with boiling water, and placed in a convenient glass apparatus; then it is calcined, a current of atmospheric air being at first passed through it, to burn off the carbon deposited by the iron. Afterwards a stream of hydrogen is passed through it, to reduce the oxide of copper which may form. It is left to cool in this apparatus, and the copper is weighed: if it be washed on a filter, and this last is burned with those portions of metal which cannot be taken up from it, a small portion of silicate of copper is obtained, the metal not being totally reduced by the hydrogen, and must be calculated as oxide, on deducting the weight of the cinders of the paper.

It is impossible to judge of the weight of the copper by the precipitate obtained with sulphuretted hydrogen; for the sulphuret oxidizes whilst drying, and becomes partially acid: but if a determined quantity is taken, which fills a small crucible warmed by a lamp, and the mass be heated so that the excess of sulphur, the moisture, and the excess of sulphuric acid be driven away, and there remains only the copper at the least degree of sulphurous combination, the weight of the copper may be calculated from the weight of this protosulphuret.

Sixth Example. Nature often affords mixtures of metallic compounds which cannot be considered as true combinations, but with whose composition it is occasionally important to become acquainted. Let us suppose such a mass containtaining sulphur, arsenic, antimony, iron, cobalt, nickel, copper, lead, and silver. In this case it is of great consequence to separate the electro-negative from the electro-positive bodies, which is not easily accomplished with exactitude by solution in acids. To perform this, a process is employed founded on the property possessed by the electro-negative bodies of forming volatile combinations with chlorine. A bulb is blown in the middle of a glass tube about 8 inches long; the pulverized material for analysis is placed in this bulb, and weighed in it. The tube is open at the end where the gas should disengage itself, and it is curved in such a way as to pass into a flask about two thirds filled with distilled water; chlorine is then disengaged, which ought to pass over chloride of calcium before coming into the tube. (Vide fig. 2.) After having passed through a sufficient quantity of chlorine to drive out the atmospheric air, the bulb is heated gently with a spirit lamp; the metals then begin to unite with the chlorine; the sulphur, the arsenic, and the antimony distil, and pass into the water. The action is slowly carried on, and should be prolonged for several hours:

there is no occasion to wait for the decomposition of the whole of the matter employed, for it is but partial; and the undecomposed parts remaining the same as before the operation, their weight can be deduced.*

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* The following is considered the best process for analysing minerals of nickel and of cobalt (arsenio-sulphurets):— The bulb B, which is situated near the middle of the tube *b*, and is destined to contain the material, ought to be sufficiently large to remain about two thirds empty; the tube is first weighed without, then with, the substance.

The vessel A, from whence the chlorine proceeds, is capable of holding somewhat more than two pints. A mixture of peroxide of manganese and marine salt is placed in it, and water is thrown over it, so as to fill at least half the flask. The tube T, furnished with chloride of calcium, is open at both extremities, and joined to B by means of a caoutchouc tube. The superfluous gas is disengaged from the flask F through the tube *t*. All being in readiness, sulphuric acid is poured in through the tube with a funnel head *e*. The mixture is heated, and the chlorine disengages itself in sufficient quantity: it is necessary to abstain from heating the flask A, for the disengagement of gas will be far too abundant. The bulb B is heated with a spirit lamp, the flame of which should not be strong; but the greatest care should be taken that the chlorine drives away all the air, the oxygen of which will make a small quantity of arsenic pass into the state of arsenious acid. The remainder of the operation requires no other attention than that of adding from time to time, and when the disengagement of gas slackens, a fresh portion of sulphuric acid. At the end of twelve hours the operation is complete.

When the current of chlorine passes sufficiently slow, the

(A) We first decompose that which remains in the bulb; the mass is removed into a glass by means of water; a little nitric acid is added, in order to favour the solution of the chloride of lead which forms, that which the acid and water leave undissolved is a mixture of chloride of silver and undecomposed matters.

(*a*) The chloride of silver is extracted by caustic ammonia; the ammoniacal solution is saturated by hydrochloric acid; the precipitated chloride of silver is washed, dried, and weighed.

(*b*) The acid solution contains the chlorides of iron, of cobalt, of nickel, of copper, and of lead. The lead is precipitated by sulphuric acid, and

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chloride of iron simply sublimes, without being carried into the curved part of the tube *b*. Nevertheless, for greater safety, a bulb less than that at B may be blown in the middle of this portion (at the part *b*); the chloride of iron which may be carried forward will collect in it. The operation being finished, part of the volatile acids still adhere to the tube *b*, from the opening of the bulb to the extremity of the tube. The tube is heated in these different parts so gently as not to volatilise the chloride of iron which may be found in them severally; a solution of carbonated alkali is then thrown through the tube *e*; the current of carbonic acid resulting from this drives away the volatile acid vapours; lastly, the curved part of the tube is dipped several times in pure water, to take off the traces of acid which may adhere, and the liquor is added to that which is found in the flask F.

the liquor, together with the precipitate, is evaporated to dryness, to drive off the free acid which would retain some sulphate of lead in solution. The dried mass is treated with water, which does not dissolve the sulphate of lead, the quantity of which gives by calculation the weight of the lead.

(*c*) The liquor is saturated with ammonia in slight excess, and the oxide of iron is precipitated with succinate of soda.

(*d*) A great excess of sulphuric acid is added to the liquor, from which the copper is precipitated by sulphuretted hydrogen, and the precipitate treated as I have directed in the preceding example.

(*e*) The remaining liquor is boiled to drive off the sulphuretted hydrogen. An excess of ammonia is added to re-dissolve the oxides of cobalt and of nickel that precipitate at first; potassa is then added until the blue colour disappears; filtration is then performed, and the oxide of nickel which remains on the filter is washed, dried, and calcined; the proportion of the nickel is determined from its weight.

(*f*) The remaining red (or slightly coloured) liquor is evaporated, so that the ammonia is driven off. The peroxide of cobalt precipitates; it is washed and dried, and is reduced to the state of protoxide by strong calcination: its weight yields that of the cobalt.

(B) The acid liquor into which the volatile portions have been received is heated so as to drive off the excess of chlorine. A mixture of antimonious acid and sulphur is found at the bottom of the flask, which is separated. The liquor contains hydrochloric, sulphuric, and arsenic acids.

(*a*) The liquor is saturated with ammonia, in order to be certain that the acids contain nothing in solution capable of being precipitated by this alkali. An excess of acid is next added, and the sulphuric acid precipitated by the chloride of barium (muriate of barytes); the arseniate of barytes that forms at the same time remains dissolved in the excess of acid. After having separated the deposit of the sulphate, the excess of barytes is precipitated by sulphuric acid, and filtration is performed. The liquor contains arsenic acid, the proportion of which is determined by the following process.

(*b*) The weights of all the other substances contained in the mineral having been determined, the sum is taken, and that which is wanting to complete the weight of the matter examined is only arsenic. From one and a half to twice its weight of pure iron (for instance, iron filings) is then dissolved in nitric acid. This solution is mixed with that of the arsenic acid, and precipitated by caustic ammonia; the precipitate is the arseniate of iron. 100 parts of iron, from which ½ per cent.

of carbon is deducted, gives 143·5 of peroxide of iron: all that the washed and calcined precipitate weighs more than the result obtained from these data is arsenic acid, which gives by calculation the weight of the arsenic.

(*c*) The sulphur mixed with the antimonious acid is separated by dissolving the latter in concentrated hydrochloric acid. The sulphur that remains undissolved is first washed with hydrochloric acid, then with water; it is weighed, and its weight added to the sulphur contained in the sulphate of barytes: the total is the quantity of sulphur contained in the mineral.

(*d*) The liquor containing the chloride of antimony is precipitated by the water. The antimonious acid is filtered, washed, dried, and calcined. The filtered liquor is reduced to a small bulk, and the antimony that it still contains is precipitated by polished iron, washed, dried, and weighed; its weight, added to that of the antimony contained in the antimonious acid, gives the whole of the antimony contained in the analyzed matter. The whole of the antimony may be at once precipitated by iron from its solution in hydrochloric acid, instead of treating it with water, in the first instance.

In the preceding examples, I have endeavoured to combine all those cases which are of most frequent occurrence. As for those that I have not been able to mention, and those complicated cases for which the above-described processes will not answer, each person ought to consult the properties of the bodies whose presence he has ascertained, and his individual resources in discovering particular methods, setting out with this general rule, that that is the best analytical process which depends least for its accuracy on the skilfulness of the operator.

In every analysis there is an inevitable loss, owing to the multiplicity of operations, which among practised chemists rarely amounts to 2 per cent., and varies generally between 1 and 2 per cent.; but which, when only two or three bodies are separated, ought not to amount to ½ per cent. This loss ought never to be corrected by a proportional augmentation of the different constituents, for it often occurs more in one body than in another; and those analyses the results of which correspond exactly to the weight of the matter employed, often deserve less confidence than those in which a greater loss is honestly acknowledged. If the loss exceed 2 per cent., without having to deduct from it a fault or a mistake committed during the analysis, it is to be presumed that the substance examined contains an alkali, or sometimes an acid, especially the hydrofluoric acid; in this last case the fossil experiences a great loss by ignition, which increases in prolonging the action of the heat. Frequently an augmentation of weight is discovered instead of a loss: this happens among inexperienced chemists, on account of the imperfect washing of the precipitates; and this is a greater fault than the losses.

In the hands of a practised chemist the augmentation of weight results from the protoxides of iron, of manganese, of cobalt, &c. contained in the mineral passing to the state of peroxide; the excess of oxygen must then be deducted. This circumstance has often been neglected, and has helped to conceal losses.

There is another cause of the augmentation of weight, when, during the precipitation of an oxide or an earth, a basic salt is formed; for example, a salt of sulphuric hydrochloric, or of another added acid, which does not become decomposed during calcination, or which does not become so except at a temperature to which bodies are seldom heated before being weighed. One may be sure that these basic salts form in the precipitations by caustic ammonia, when it has not been added in excess, and when the liquor is not allowed to macerate for some time with the precipitate. I have said above, that when minerals containing alumina are treated with potassa, too great a weight of alumina is generally found, because this last retains some potassa. In summing the results of an analysis, the attention should be especially fixed upon the accordance of these results with the chemical proportions. When this accordance fails, the result of the analysis ought to be regarded as faulty, and the cause of error should be sought. When the result of analysis is directly opposed to the law of chemical proportions, care should be taken in citing it as an exception to these laws, or as a proof against their justness, — an exposure which will only show ignorance of the difficulty of obtaining exact results. Moreover, a like discordance may happen when the analysis has not been made with a pure specimen, or when a purely mechanical mixture is used. This disagreement also sometimes occurs when isomorphous bodies are examined, crystallized together; but not contracting any chemical combination in fixed proportions.

The quantitative examination of the gases that enter into solid bodies is performed in different ways. The gas is driven off by means of an acid in the moist way; for instance, the carbonic acid by the sulphuric or nitric acid; or otherwise it is driven away by calcination. In the first case, a glass matrass is weighed with dilute nitric acid deprived of nitrous gas. The mineral for analysis is weighed in thick pieces of tolerable size, which are gently placed in a matrass so as to avoid splashing; the matrass is inclined, and a glass tube containing chloride of calcium, previously calcined to redness, is weighed and adapted to its neck. The gas deposits all the water in this tube; and at the end of the operation the last residue of gas can be driven away by heat, unless a loss of water is to be feared. That which the whole apparatus weighs, minus the weight of the matrass, of the acid, the mineral, and the tube, with the chloride of calcium, is the weight of the disengaged gas.

When a gas is dissipated by calcination, a small distilling apparatus is used, similar to that in which minerals are calcined, to ascertain the quantity of water they contain. The following is the mode in which the operation is performed, in order to drive off the water and gas at the same time: a bulb of a convenient size is blown at the extremity of a glass tube, and the mineral weighed in it. The tube is then drawn out at a small distance from the bulb into a narrower tube, and curved at the same time, so that the whole resembles a small retort with a narrow neck; it is then weighed again, so that the weight of the mineral being known, that of the little retort is obtained. A receiver open at both ends is blown for this retort; the neck of the retort is introduced into one of the openings of the receiver, and joined by means of a caoutchouc tube; the other end terminates in a small tube containing chloride of calcium. The receiver and the tube containing chloride of calcium are weighed; the gas and the water are driven off at once by the heat: but as the gas only is lost, it is easy to ascertain its weight by the diminution in the weight of the whole apparatus; that which the little retort weighs less than before is equal to the total weight of gas and water. A drop of water generally remains in the neck of the retort; in this case the neck is cut beyond the place where the drop is found,—without, however, detaching it from the receiver,—after which they are weighed together; the neck of the retort is next taken out of the receiver, it is dried, and its weight deducted from the preceding weight. The increased weight of the receiver, and the tube containing the chloride of calcium, is that of the water; whose weight, added to that of the disengaged gas, should answer to the loss that the apparatus has sustained weighed with the end of the dried neck.

If the gas to be driven off is ammonia, the tube should be filled with fused potassa, and deprived of its water of crystallisation, for the chloride of calcium absorbs ammonia. Analytical examinations for determining the gas and water are necessary in the analysis of manganese, metallic carbonates, &c.

GENERAL RULES FOR THE ANALYSIS OF GASES.

When the analysis of a gas is desired, it must be received over mercury as soon as possible. The insoluble gases can be received over water, and in this way results sufficiently exact may be obtained, making the necessary corrections for the presence of aqueous vapour; but it is always a surer mode to receive them over mercury, and it is absolutely necessary to do so in delicate experiments. In the examination of gaseous mixtures, first the volume of the mixture, and, secondly, the quality and relative volume of the constituents must be examined.

To determine the bulk a cylindrical tube is used, graduated in decimal divisions of cubic measure, observing that the interior and exterior levels are equal, and noting the state of the barometer and thermometer; the thermometer being for some time suspended in the graduated tube. The volume of gas at the given pressure and temperature being determined, they must be reduced by calculation to a mean temperature and pressure; for example, 0.76 pressure and 0° temperature.* It is much to be desired that all chemists should reduce their results to these fixed points, so as to be able to compare without difficulty the results of different examinations.

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* The 0° of centigrade = 32° Fahrenheit. In this country gases are examined at 60° Fahrenheit, and thirty inches' barometrical pressure.— *G. O. R.*

In order to determine the nature of the gases that compose a mixture, the following re-agents are employed:—

a. Hydrogen is used when the presence of oxygen is suspected in the mixture, or this latter gas when the mixture contains inflammable gases: the operation is performed in the eudiometer. If the mixture contain such small quantities of hydrogen or oxygen that they will not detonate, a mixture of hydrogen and oxygen, in which one or other of these gases is in excess, according to circumstances, must be introduced in known proportions. After having passed the electric spark, it is observed whether the condensation be greater than it should be according to the proportion of the mixture; if it be so, a portion of the primitive gas under analysis has been exploded.

b. A solution of neutral protosulphate of iron, or, what is better, of protochloride of iron. This dissolves nitrous gas readily, assuming a black or dark-brown colour.

c. A solution of the neutral acetate of lead is darkened by the contact of combustible gases containing sulphur or phosphorus.

d. Barytic, or lime water, absorbs carbonic acid, becoming opaque, as also sulphureted hydrogen, without this effect being produced.

e. Peroxide of lead absorbs sulphurous acid.

f. Soda, or hydrate of potassa, absorb all the acid gases. Cyanogen is also absorbed by these alkalies, and renders them black or brown when it is in excess,—a colour which is dependent on its decomposition.

g. Borax absorbs all the acid gases except carbonic acid and sulphureted hydrogen.

h. Chloride of silver absorbs ammonia, sulphureted hydrogen and phosphureted hydrogen, and disengages hydrochloric acid, by the action of these two last, without acting upon other gases.

i. Fused chloride of calcium and crystallised boric acid absorb ammonia, and leave most of the other gases.

k. Crystallised boric acid absorbs fluosilicic acid gas.

l. Chlorine condenses olefiant gas, and empyreumatic oily vapours, when in the dark, and leaves the protocarbureted hydrogen for condensation, for which purpose the daylight is necessary. In the sun an explosion takes place with the chlorine, the excess of which gas is removed by potassa.

m. Potassium separates carbonic oxide from carbureted hydrogen: when heated in the gaseous mixture it oxidises at the expense of this gas, and entirely condenses it.

n. Incombustibility and the absence of all positive signs denote the presence of azote.

o. The composition of a gaseous mixture is often tested by introducing into it papers steeped in different re-agents: blue paper or red turnsole paper, to discover whether the gas be acid or alkaline; paper dipped into a solution of sulphate of iron, to know whether the gas contain hydrocyanic acid, &c. &c.

As to the quantitative analysis of gases there is no other rule than that of employing the beforementioned re-agents successively, and of concluding the quantity of each gas from the absorption they produce. The analysis of gases performed by a person sufficiently practised in its execution affords the surest results; for the mistakes are seldom so great, but that, on comparing the relative volumes of the gases, the true results are perceived, conformable to the laws of chemical proportion: but if, during an analysis, part of the elements is determined by weight and another by the measure of gases and their reduction into weights, greater faults may be committed than if the result had been obtained entirely from weights. Cases, however, occur in which one is obliged to proceed thus,—cases in which not only extreme precision is necessary, but also a precise knowledge of the density of the gas whose weight is to be determined.

ANALYSIS OF MINERAL WATERS.

The employment of these waters in medicine has given the greatest interest to this branch of analysis. The substances generally met with in the waters from Swedish springs are the chlorides of sodium and potassium, the chlorides of calcium and magnesium (rarely a small proportion of alkaline or calcareous sulphates), the alkaline carbonates, the carbonates of lime, magnesia, of protoxide of iron, sometimes of protoxide of manganese; moreover, they all contain silica, dissolved without the assistance of an acid or an alkali. To the salts before named may be added, with regard to the waters of great towns, the nitrates of potassa, of lime, and of magnesia. When these waters re-act, as if containing free acid, it is owing to the presence of a small quantity of carbonic acid, which is then the solvent of the earthy carbonates. Some waters also contain sulphureted hydrogen; but in such small quantity that its presence can be discovered only by partly filling a glass, covering it with the hand, and shaking it violently; after which, the uncovered glass being quickly carried to the nose, a slight smell of sulphureted hydrogen is perceived.

Most of the Swedish waters contain likewise a portion of that soluble substance which forms part of the soil, and which is generally called extractive matter. Usually they do not contain sufficient to become coloured, at least when the volume of water is not greatly reduced by boiling, in which case they at last assume a brownish-yellow colour. Some waters contain sufficient of this matter to be coloured in their natural state; for instance, the water of Porla, the colour of which is brownish yellow. Our mineral waters contain, besides, azote, without oxygen, which latter has been absorbed by the iron or extractive matter during their course.

They generally contain such a quantity of azote as is found in a water impregnated with atmospherical air, but whose oxygen has been absorbed without being replaced by azote.

This property varies in proportion to the distance of the water from its source.

The nature of the substances dissolved differs much in these waters; for instance, the spring of Loka contains water from the purest source at present known. The fountains of Stockholm contain a great quantity of nitre: the spring of Runnaby contains protosulphate of iron. Our common mineral waters, for instance, of Medevi, of Saetra, of Ramloesa, Porla, contain protocarbonate of iron, some with, others without, alkali.

The springs of Stockholm, as well as that of Saint Ragnildo near Sœderkœping, are common springs, which only differ in containing more earthy carbonates.

In other countries, especially in Germany, there are springs highly charged with foreign matters: many contain a quantity of carbonic acid equal to the volume of water; for instance, the waters of Seltz, of Pyrmont, and of Faching. Others contain great quantities of sulphureted hydrogen, mixed with carbonic acid and azote; as the waters of Aix-la-Chapelle. The quantity of salts contained in these waters is very great compared to the Swedish waters. The waters of Faching, of Geilnaw, and of Seltz, contain much carbonate of soda, whilst the waters of Pyrmont, of Meinberg, and of Spa, contain a great quantity of carbonate of iron.

The waters of Seidlitz and of Seidschutz contain great quantities of sulphate and hydrochlorate of magnesia, &c.

The mineral waters are divided into four classes, ferruginous, alkaline, saline, and hepatic waters.

Many waters may belong at the same time to several classes; they are then arranged according to the character which predominates.

The following are the names of some of the most celebrated waters: —

First. — Ferruginous waters.

- *a.* Waters purely ferruginous, viz. Medevi, Pyrmont.
- *b.* Alkaline ferruginous waters, viz. Porla, Saetra, Ramlœsa, Adolfsberg, Spa, Eger, Marienbad.

Second.—Alkaline waters, viz. Carlsbad, Marienbad, Bilin, Faching, and Seltz.

Third.—Saline waters viz. Seidschutz, Seidlitz, Epsom, and Pyrmont.

Fourth.—Hepatic or sulphurous waters, viz. Aix-la-Chapelle.

I am here going to give some rules for the analysis of mineral waters which I have often had occasion to practise upon those of Sweden. The qualitative analysis is performed by means of the re-agents, as will be seen. By these means it is easy to discover the nature of the substances that a water contains; and an experienced eye may at once conclude, by the greater abundance of the precipitates, the greater or less quantity of the different matters contained in the fluid.

EXAMINATION OF MINERAL WATERS BY RE-AGENTS.

We should observe,

a. The colour and transparency of the water.

b. Its smell, according to the method above mentioned, for discovering the presence of sulphureted hydrogen.

c. Its taste, which may be saline, bitter, or like that of ink; it must be remembered, however, that the disagreeable taste which some springs appear to have in the morning, which is not discoverable during the day, signifies nothing, for it is dependent on the variable conditions of the organ of taste.

d. In the following way it may be ascertained whether a water contain a less or greater portion of volatile substances. A bottle is filled with the water destined for examination, and half emptied; the mouth is then stopped with the thumb, the bottle is shaken strongly for some minutes, and then turned with the neck downwards, and the thumb is withdrawn sufficiently to see whether any water escapes which may be received in a glass in order to determine its quantity. Care must be taken to hold the bottle in such a manner that it may not be heated by the hand during the agitation, so that the dilatation only of the air contained in the bottle may not occasion an erroneous result.

These trials having been made, if possible at the spring, the analysis is continued, by re-agents, as follows:—Thirteen glasses are taken, ten are filled with the fresh water for examination, and three with prepared water that has been boiled at least for half an hour, and that has been filtered after cooling. The following re-agents are next dropped into the glasses:—

First.—Tincture of turnsole (prepared with cold alcohol and cakes of turnsole: alcohol preserves the tincture unaltered for a length of time). When the water into which a few drops of this tincture have been thrown assumes a red shade, the presence of a free acid must be concluded: if, on the addition of a greater quantity of tincture, the reddish liquor assumes a bluish tint, the quantity of acid is small; and if the reddened water becomes blue again after from twelve to twenty-four hours, and the tincture of turnsole added to one of the glasses containing the boiled mineral water does not become red, the acid contained in the water was the carbonic: a dark permanent red colour denotes the presence of a metallic salt.

Second.—Lime water saturates free carbonic acid, so as to occasion a precipitate of neutral carbonate of lime: the earths and metallic oxides which had been dissolved in the carbonic acid precipitate at the same time. If the water contain free carbonic acid, the precipitate is redissolved by the addition of a sufficient quantity of this water. In order to make the experiment well, it is commenced by allowing a few drops of lime water to fall into the water: the troubling which is at first occasioned afterwards disappears. If the water do not contain free carbonic acid, but only bicarbonates, the troubling caused by the lime water does not disappear, whatever quantity of the mineral water may be added. The majority of Swedish waters that I have examined, containing carbonic acid, act in this manner.

Third.—The tincture of Brazil wood passes from a yellowish brown to a beautiful red when the mineral water contains an alkali or an earthy carbonate.

Fourth.—The chloride of barium precipitates a sulphate of barytes. An alkaline water ought to be mixed with acid, before adding the barytic solution to it, so as to prevent the re-action of the alkali on the barytic salt: few Swedish waters contain sulphates in considerable quantity.

Fifth.—Nitrate of silver indicates the presence of the chlorides which precipitate it in the form of a white and thick cloud. If in the first instance the precipitate is black or brown, the presence of sulphureted hydrogen may be concluded. Sometimes after a short interval the supernatant liquor assumes a wine-red colour, still preserving its transparency. This effect, according to the experiments of M. Hermbstaedt, is owing to the presence of an acid and volatile body, which he supposes to be the sulphureted or phosphureted hydrogen: he has found it both in the water of the Baltic Sea, and in that obtained from it by distillation.

Sixth.—Oxalate of ammonia and the acid oxalate of potassa precipitate an oxalate of lime which deposits slowly.

Seventh.—The subphosphate of ammonia added to the filtered liquor shows the presence of magnesia.

Eighth.—Caustic potassa precipitates the earths and metallic oxides from their solution in acids. A white precipitate, which after some time becomes yellow, indicates the presence of iron, or else of a certain quantity of extractive matter that colours the precipitate.

Ninth.—Bicarbonate of potassa precipitates the earthy and metallic oxides, when dissolved in any other acid than the carbonic.

Tenth.—Ferro-cyanuret of potassium gives a green colour to alkaline ferruginous waters, and a greenish-blue precipitate deposits after some hours. If the water be not alkaline, or when the alkali has previously been saturated with an acid, the precipitate immediately assumes a blue colour. In the previously boiled water the ferro-cyanuret of potassium does not react when the iron has been held in solution by the carbonic acid.

The red ferro-cyanuret is still more sensible than the yellow one, because the springs contain iron in the state of protoxide, with which this last re-agent immediately forms a blue precipitate.

Eleventh.—The neutral deutochloride of gold produces a troubling in ferruginous waters, according to M. Ficinus; causing a precipitate of metallic gold, which is visible even in waters on which the prussiate of potassa and gall-nut produce no effect; but it is necessary that the free acid should be first saturated by carbonate of soda.

Twelfth.—Gallic acid, or, in lieu of this, the alcoholic infusion of nut galls, does not at first produce any change in a ferruginous water just drawn, but after some time the water becomes gradually coloured. A clear purplish colour, which does not increase after some hours, indicates an exceedingly small quantity of iron. Our ferruginous waters generally give a very dark purple colour; and those which contain more iron assume a blackish-brown colour. Waters that contain much alkali give a dirty colour, between green and dark brown. Waters containing so little iron that its presence cannot be demonstrated by tincture of galls alone re-act sensibly, according to Mr. Philips, when a little lime water, or, what is better still, a solution of carbonate of lime in carbonated water, is added to them.

When gallic acid does not produce a purple colour in the boiled water, the protoxide of iron has been held in solution by the carbonic acid; and if the boiled water assumes, after some hours, a sea-green colour with the gallic acid, it contains some alkali.

This re-action is so delicate, that it serves to demonstrate the smallest quantities of alkali; but for that purpose it is necessary that the water should have been boiled some length of time, for otherwise the alkaline re-action may be owing to the presence of carbonate of magnesia.

A crowd of other re-agents exist, but their employment has never taught me any thing new; and those that I have enumerated have always sufficed.

By collecting together the substances detected by the preceding experiments, those that can be combined are easily known; and as they are to be united according to the affinities ascertained to be strongest, it is easy to indicate, with tolerable certainty, what were the salts dissolved in the water.

ANALYSIS OF THE SOLID PARTS OF THE WATER.

A certain quantity of the water is weighed or measured, placed in a glass or porcelain capsule, covered by paper, and evaporated at a gentle heat, which ought not to be raised to the boiling point: in this way the mass is reduced nearly to dryness. If the water contain a great quantity of gas, it is necessary to leave it in the open air for forty-eight hours, or else to cover it over at the commencement of evaporation with a glass, from which the particles projected by the effervescence may be made to fall by washing.

It is useless to be at the trouble of evaporating to perfect dryness to obtain the weight of the salts; for this attempt is fruitless, on account of the difficulty experienced in withdrawing the mass from the vessel without loss, if the vessel be not of such a size that it can be weighed first with the saline mass, then alone. But much is not gained in any case, for the mass retains moisture, and cannot be perfectly dried, unless the extractive matter be destroyed, so that the result of the weighing does not give any satisfactory result.

First. — The mode of examining the dry mass varies, according as it contains free alkali or earthy salts: the latter alone are the cases I am about to describe.

(A) Alcohol is thrown on the mass, macerated for some hours, and filtered on a weighed filter: to make the saline mass fall on the filter, the feather of a pen and alcohol are used. The mass is next washed on the filter with boiling alcohol so long as it dissolves any thing. The alcoholic solution contains the chlorides of potassium, of sodium, of calcium, and of magnesium, the extractive matter, which gives it a red or yellowish-brown colour, and a resin in some instances which appears to vary with the springs.

The alcohol is evaporated on a balanced glass capsule, and the residue is weighed; it is again dissolved in alcohol: the resin remains behind.

When the water contains earthy chlorides, which almost always happens when it does not contain an alkali, the earths are precipitated by boiling with carbonate of soda; but it is well to add a few drops of caustic ammonia before hand: if this cause a precipitate, it will be phosphate of lime or some true earth: this may be ascertained by the examination of the precipitate; and if it be composed of lime and magnesia, these two earths are separated by the mode described in the second example on the analysis of minerals.

The liquor precipitated by carbonate of soda is saturated with nitric acid, and precipitated by nitrate of silver. The precipitate is collected on a weighed filter, washed, and dried completely: the weight of the hydrochloric acid is deduced from the weight of the precipitate.

The presence of potassa is next sought in the liquor from which the hydrochloric acid has been precipitated; for this purpose the excess of nitrate of silver is precipitated by a little hydrochloric acid or marine salt (chloride of sodium): the liquor is filtered, and evaporated until crystallization commences; it is then mixed with the double salt of soda and platina, as I have above directed in the third example. The quantity of potassa, lime, magnesia, and hydrochloric acid, is now ascertained.

The quantity of hydrochloric acid requisite for the saturation of these bases is ascertained by calculation; and by the deduction of this quantity from the total weight of the hydrochloric acid the portion of acid united to the soda may be known, and consequently the weight of the soda: in this manner, therefore, the quantity of each of these four salts may be determined in the anhydrous state.

It is true that the extractive matter dissolved in alcohol is lost: but it is impossible to determine its proportion with exactitude, since it mixes itself throughout; besides, the determination of it is of very little interest at present.

(B) Lukewarm water is thrown upon those portions remaining in the capsule, and the whole is added to the residue left by the alcohol on the filter; and the addition of warm water is to be continued so long as the filtering liquor holds any thing in solution. That which now dissolves consists of the sulphates of lime, magnesia, and soda, rarely that of potassa. A drop of ammonia is first added to the liquor, and if a precipitate forms, it must be examined apart: the earths are next precipitated by carbonate of soda, and the quantity of sulphuric acid is determined by the chloride of barium; after which the calculation is made, as we have before directed, for the chlorides of these bases.

(C) If the salts soluble in alcohol contain nitrates also, the analysis becomes complicated.

When the weights of the bases and of the hydrochloric acid have been determined, it may be admitted that the quantity of nitric acid suffices for the saturation of the excess of the bases. Another mode of determining the quantity of nitric acid is that of mixing a given weight of the salts, soluble in alcohol and water, with copper filings and hydrochloric acid, the deutoxide of nitrogen that evolves is collected, and the weight of the nitric acid is concluded from its volume; or else the quantity of the dissolved copper is determined, and the portion of decomposed nitric acid is calculated from it. If the alcoholic solution contain nitrates, the salts insoluble in alcohol always contain the nitrate of potassa, a circumstance to which particular attention must be paid.

(D) With respect to the waters that contain gypsum (sulphate of lime), the parts insoluble in cold water should be boiled for some time with three hundred times their weight of water: this ebullition is best performed by small portions. The solution of sulphate of lime thus obtained is evaporated, and the salt calcined in a covered platina crucible: the mass generally has a yellow colour before the calcination, owing to the presence of a portion of extractive matter.

(E) The portions which cannot be removed from the capsule, either by alcohol or by the water that is afterwards added, are detached by means of hydrochloric acid, which dissolves the portions insoluble in water, remaining on the filter (vide B). It is often useful to calcine the mass before solution to destroy the remaining extractive matter. The hydrochloric solution contains iron, manganese, lime, and magnesia, that are to be separated by the mode we have above described. Some waters contain carbonate of strontian, fluoride of calcium, the phosphates of lime and of alumina; for instance, the waters of Carlsbad, of Kœnigswart, and of Eyre in Bohemia. The strontian is obtained, together with the lime, from which it is separated, on treating the two earths with nitric acid, evaporating to dryness, and digesting the residue with pure alcohol, which does not dissolve the nitrate of strontian. The presence of hydrofluoric acid is ascertained by dissolving the earths in an excess of nitric acid, and evaporating the solution to dryness in a platina crucible covered with a watch glass: after the desiccation the traces of hydrofluoric acid are visible on the glass; but it is impossible to determine the quantity of this acid with any exactness, especially as it is generally very small, and the presence of silica complicates the operation. When the quantity of hydrofluoric acid is not very small it can be determined in the following manner:—The residue insoluble in water is dissolved in very dilute nitric acid, filtered and washed several times with a little water, after which a few drops of a solution of potassa are added to the acid liquor, which ought not to be concentrated by evaporation, care being taken not to saturate the whole of the acid. After some time a gelatinous deposit forms, which is thrown on a filter and washed with alcohol: strongly dried, the fluosilicate of potassa so obtained contains 29·4 per cent. of hydrofluoric acid, and 28·47 of silicic acid. The earthy phosphates are precipitated by ammonia, together with the peroxide of iron: the alumina is separated by caustic potassa, which also seizes on its phosphoric acid: the phosphate of lime is obtained by separating the iron either according to Mr. Herschel's method, quoted in the first example, or by a solution of ferro-cyanuret of potassium, as we have above mentioned. The hydrochloric acid leaves the silica, which often enters, proportionally to other substances, in considerable quantity in our spring waters.

Second. — The analysis of alkaline waters is more simple; they are evaporated to dryness: the salts thus obtained are calcined and weighed, after which they are saturated with acetic acid. The sulphuric acid is next precipitated by the acetate, or nitrate of baryta, and after having separated the precipitate the water is treated with nitrate of silver. It must be remarked, however, that before the precipitation by nitrate of silver, it is proper to add nitric acid, in order that the acetate of silver may not precipitate. If nitric acid be added at the commencement of the operation, it will be difficult to separate the sulphate of baryta from the whole of the nitrate of this base. From these data it is easy to calculate the quantity of sulphates and chlorides contained in the mixture of salts. The overplus is an alkaline carbonate. These waters sometimes contain phosphates, which are discovered, when, after the precipitation of the excess of nitrate of silver by hydrochloric acid, the liquor is supersaturated with ammonia in a well corked flask: phosphate of baryta with excess of base then precipitates. Should it be now wished to ascertain the presence of the alkali the liquor is evaporated to dryness, and the salt so obtained is digested with a solution of carbonate of ammonia, which does not dissolve the baryta. The clear liquor is evaporated, and the calcined salt is treated, as above stated, with the solution of platina.

Before quitting the analysis of waters by evaporation, I ought to mention a compound that frequently exists in sulphurous waters; Mons. Basse and Westrumb discovered it in the sulphurous waters of Hameln, in 1805, and have called it "resine puante." The water is evaporated in a retort furnished with a receiver; alcohol is thrown on the mass, which has been evaporated nearly to dryness. The alcohol dissolves this resin, and the salts soluble in this liquid. The alcoholic solution is separated, mixed with a little water and distilled. After having driven off the alcohol this resin remains in the form of a yellowish oil on the surface of the water. This oil becomes decomposed in the air, at the same time depositing sulphur, and becomes transformed into a resinous and carbonaceous matter, that has a very disagreeable odour, and is not precipitated by water from its alcoholic solution, but dissolves with difficulty in the water. The alcoholic solution of this substance re-acts as an acid.

This "resine puante" is composed of a resinous mass united to sulphur and sulphureted hydrogen, and is analogous to that obtained by melting oils or resins with sulphur. It is asserted that it can also be obtained by dissolving sulphuret of potassium in boiling alcohol: precipitating the potassa and sulphur by a quantity of sulphuric acid sufficient for the saturation of the potassa, mixing the filtered liquor with a little water and distilling it. The alcohol is decomposed, and this resinous sulphureted matter is formed.

It is thought that it is produced in the interior of the earth by the sulphur of the sulphuret of iron and naphtha.

EXAMINATION OF THE GASES CONTAINED IN MINERAL WATERS.

A known quantity of water for examination is put into a round bottle, capable of containing 100 to 200 cubic inches, leaving, unfilled, only two cubic inches in the neck. The mouth of the bottle is closed with a good cork stopper, furnished with a tube to let off the gases, which is inserted into a flask capable of containing fifty cubic inches, four fifths filled with lime water and caustic ammonia. The tube should reach nearly to the bottom of the vessel, and all access of air between the tube and the opening of the flask should be prevented by a loosely fitted cork. The bottle is plunged some inches in a sand bath, and heated by degrees until the water boils, and the boiling should be continued for an hour. When the water approaches the point of ebullition, the gas begins to come off, and the lime water absorbs the carbonic acid, occasioning a precipitate of carbonate of lime. The ammonia acts in such a way that the carbonic acid is not carried off by the aqueous vapours without being absorbed. When the vapour of the water that distils does not appear to contain gas, which is easily seen by the perfect condensation produced, the flask is removed and corked, and when all the carbonate of lime has deposited, the greater part of the supernatant liquor is removed by a syphon. The carbonate of lime is thrown on a filter. It often happens that a part of the carbonate crystallises on the inner surface of the flask and adheres strongly. This adherent residue must be well washed to free it from lime water, afterwards it is dissolved in hydrochloric acid, and precipitated from the neutralised solution by oxalate of ammonia. This precipitate is thrown on the filter that contains the carbonate of lime: it is washed, dried, and calcined, and the quantity of carbonic acid is calculated in weight and volume from the weight of the carbonate of lime.* In order to ascertain the presence of sulphureted hydrogen, nitrate of silver, which has first been saturated by ammonia, is added to the water. The black precipitate that forms when the water contains sulphureted hydrogen, and which is sulphuret of silver, gives by calculation the quantity of sulphureted hydrogen. The quantity of atmospherical air, or of azotic gas, is ascertained by filling the bottle and the tube that transmits the gases with the water for examination, so that no more free air remains, and by receiving the air that disengages itself during ebullition in an inverted vessel containing lime water or a weak solution of caustic of potassa. The gas thus obtained is measured in a graduated tube, and its nature determined according to the rules laid down for the analysis of gases.

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* The oxalate of lime is converted into carbonate by the calcination.

Most of the Swedish waters that I have examined contain carbonic acid and the proportion of nitrogen generally contained by these waters. The spring of Porla is an exception, for it contains no trace of oxygen, and is so impregnated with azote, that this gas rises in the form of bubbles, of greater or less size, as the water recedes from the spring and the pressure diminishes: the bubbles disengaged are a mixture of seven parts of azote with one of carbonic acid, and a little carbureted hydrogen: it is, however, probable, that the carbonic acid only mixes itself with the azote during its ascent; for the water does not contain as much carbonic acid as it might retain at its temperature, which ought to happen if the pure carbonic acid gas rose from the soil of the spring in the form of bubbles.

ON THE GENERAL CHARACTERS OF SALTS, AND RULES FOR THEIR ANALYSIS.

Rules for obtaining a Knowledge of Salts from the Reaction of their Acids.

(A) Oxy-salts.*

1. *Sulphates.* Their characteristics consist of those belonging to the radical, and those which appertain to the acid. The former are found in all salts with sulphureted acids, the latter are characteristic of sulphuric acid. The phenomena which result from the presence of sulphur are the following: — The salt, mixed with charcoal powder, and heated in a closed vessel, is transformed into a sulphuret: this is what happens to the alkaline sulphates, and many metallic sulphates; or else the salt disengages sulphurous acid, which volatilizes, and the base remains in the state of oxide: this is what takes place with the sulphates of magnesia, the earthy sulphates, and some metallic sulphates. When a sulphate is operated on whose base is capable of forming a less oxygenated salifiable oxide, a sulphuret and sulphurous acid are obtained at the same time. In order to discover the presence of sulphur in a positive man-

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* Salts formed by the combination of acids with oxygenated bases.

ner, the following experiments are performed:— The matter for examination is mixed with carbonate of soda, and the mixture heated on charcoal in the reduction flame of the blow-pipe. A portion of sulphuret of sodium then forms, in which the presence of sulphur is known by cutting off the charcoal at the place where the fused mass is found, placing it on a piece of silver, and throwing a few drops of water on it. The sulphur immediately darkens the silver; when the quantity of sulphur is very small, the metal becomes brown after a short time. A few drops of acid may also be thrown upon the fused mass that is found on the charcoal; a very sensible odour of sulphureted hydrogen then developes itself. Another method, discovered by Gahn, suffices to discover very small quantities of sulphur, especially in some minerals that do not contain metals. It consists in fusing the matter for examination in the reduction flame with carbonate of soda and a small piece of glass, which, to succeed well, should first be fused together with the soda. A sulphuret of sodium is then obtained, dissolved in the glass, which is colourless while hot, and becomes yellow, or red, during refrigeration. If only a small quantity of sulphur be present, the glass remains transparent; in the contrary case, it becomes entirely opaque.

The characteristics of sulphuric acid are the following:— The dissolved salt, mixed with a solution of a barytic salt, gives a precipitate of sulphate of baryta, insoluble in water and acids. The sulphates insoluble in water are soluble in hydrochloric acid, and precipitated by a solution of chloride of barium. It must be observed that, in this case, the latter salt is precipitated by all strongly acid solutions, and, consequently, that the acid solution should be very dilute before the chloride of barium is added. The insolubility of the precipitate in acids should be tried apart; for greater certainty, the precipitate may also be heated in the manner I have just described for ascertaining the presence of sulphur.

Sulphuric acid forms acid salts with a few bases, in which the quantity of acid is doubled. It forms many salts with excess of base, in which there are thrice, six times, and occasionally twice the quantity of base that is in the neutral salts.

2. *Hyposulphates.* In the solid state these salts are known by disengaging sulphurous acid on calcination, leaving a residue of neutral sulphate. When the solutions of these salts are boiled with sulphuric acid, they disengage sulphurous acid without depositing sulphur, and without troubling the liquor.

3. *Sulphites.* They have a particular smell, peculiar to sulphurous acid, which is likewise perceivable when the salts exist with an excess of base. Sulphuric acid disengages sulphurous acid

from them without the assistance of heat, and without altering the transparency of the solution. Dissolved in water, they absorb oxygen from the air, and pass to the state of sulphates. Heated in the solid form in an alembic, they are decomposed in such a way, that three fourths of the salt pass to the state of sulphate, and one fourth to metallic sulphuret. It is for this reason that these salts detonate slightly with nitre. Sulphurous acid appears to form neutral salts with the alkalies, which contain double the quantity of acid found in its neutral combinations with the alkaline earths; it resembles many other weak acids in this respect, viz., the carbonic, molybdic, and tungstic.

4. *Hyposulphites.* Calcined in closed vessels, one half of these salts passes to the state of sulphate, whilst the other half is transformed into metallic sulphuret. Mixed in solution with hydrochloric acid, they disengage sulphurous acid, known by its odour, and give a deposit of sulphur immediately, or after a short interval: on heating the solution the precipitate forms very quickly. They may also be known by their dissolving recently precipitated chloride of silver, assuming a saccharine taste. A solution which does not contain any sulphate, but an hyposulphite, gives, when mixed with a solution of nitrate of silver, a white precipitate, which soon becomes brown, and finally black. On this account, M. Pfaff regards nitrate

of silver as a very sensible reagent on the hyposulphites. When these salts are found mixed in a solution with sulphosalts, or with a soluble sulphuret (liver of sulphur), it is not easy to ascertain their presence. The non-oxygenated sulphur must then be precipitated by a salt of lead or copper, for these bases form soluble salts with hyposulphurous acid; they are then tested with hydrochloric acid, as I have just stated.

5. *Nitrates.* Mixed with powdered charcoal, or with any other combustible body, they detonate on being heated; in solution, their presence is ascertained by mixing the solution with hydrochloric acid, adding gold leaf and heating it; the gold dissolves and the liquor becomes yellow, but as this effect may also be produced by the chlorates and iodates, the following test must be likewise employed: — A small quantity of protosulphate of iron is dissolved in water, mixed with sulphuric acid; the liquor to be examined is added, and some copper chips placed in it. If the solution contain nitric acid, it assumes a dark colour after a short time, owing to the reduction of the nitric acid, by the copper, to the state of deutoxide of azote, which dissolves in the protosalt of iron, and colours it.

Nitric acid does not form acid salts, but salts with excess of base, which contain twice, thrice, and six times as much base as the neutral salts.

6. *Nitrites* (*hyponitrites*). These give, in part, the same reactions as the nitrates; but the mixture with hydrochloric acid does not dissolve gold; in a concentrated state the solution appears yellow, but on dilution the colour disappears. The nitrites, treated with sulphuric acid, disengage red vapours of nitrous acid even when cold, whilst, under the same circumstances, the nitrates produce white vapours of nitric acid. Solutions of nitrites disengage the deutoxide of azote slowly when boiled in distilling vessels: they then become transformed to nitrates; two thirds of the azote disengages itself in the form of deutoxide of nitrogen, whilst one third is transformed into nitric acid: with the contact of air they change, during ebullition, into neutral nitrates. No acid nitrites are known. In the basic salts, there exist twice or four times as much base as in the neutral.

7. *Phosphates.* The presence of phosphorus in the solid state is known by fusing a little of the salt with boric acid on charcoal, by means of the blow-pipe; when the mass no longer swells, and the glass quietly subsides, a small piece of iron wire is added to it; then the bead is heated as strongly as possible. The phosphoric acid is reduced; the phosphorus forms a phosphuret with the iron, which fuses into a globule; the glass is left to cool; it is broken, and the phosphuret of

iron withdrawn with the point of a magnetic knife. If the salt does not contain a sufficient quantity of phosphorus to fuse all the iron, the iron wire will be enlarged at the place where the fused phosphuret is found, which should not be confounded with the roughness of the iron produced by the oxidation of its extremities and preservation in the centre, in cases where salts do not contain phosphoric acid. If the phosphate be in solution, the phosphoric acid is discovered by the addition of lime water, which gives a white, flocculent, almost gelatinous precipitate; this is phosphate of lime, which is to be treated before the blow-pipe with boric acid and iron wire. Metallic salts, insoluble in water, or salts whose reduction might confuse the results, are dissolved or mixed with hydrochloric acid; after which, the cold acid liquor is saturated by recently precipitated hydrated oxide of iron; it is next filtered and boiled. A salt of iron with excess of base then precipitates, which contains phosphoric acid; its presence is demonstrated as above by means of the blow-pipe.

M. M. Vauquelin and Thénard have given the following method for establishing the presence of phosphorus in a salt. Potassium is placed at the bottom of a closed glass tube; the material for analysis, well dried, is added, and heat is applied; the excess of potassium sublimes. On cooling, mercury is thrown into the tube; it is gently heated, so that the potassium combines with it, and the mass is turned out; moist air is then blown on it, and the mass is removed after some moments; if it contained phosphorus, it will give out a strong smell of phosphureted hydrogen.

Another means of knowing the phosphates consists in their giving from their neutral solution a white precipitate with nitrate of lead, which fused before the blow-pipe assumes, at the moment of congelation, crystalline facettes; a property peculiar to phosphate of lead.

Phosphoric acid combines with bases in more proportions than any other acid except the arsenic, which resembles phosphoric acid in this respect. It forms, on the one hand, acid salts, in which the quantity of acid is 1⅓, 1½, and twice as great as in the neutral salts; and, on the other hand, salts with excess of base, which contain 1¼, 1⅓, 1½, 2, 2½, and 3 times more of base than neutral salts: nevertheless, the acid combines only with certain bases in these proportions, and many of these combinations are not the production of art, but of nature. Most frequently there exists twice as much of acid, and 1½ more of base than in neutral salts, in which the oxygen of the acid is to that of the base, as five to two.

8. *Phosphites.* As regards the presence of phosphorus, these salts react like the phosphates;

but they differ from them in yielding, on calcination, phosphorus or phosphureted hydrogen, which enflame and leave a residue of phosphate. Their solutions have an alliaceous smell of phosphorous acid; they reduce solutions of gold, silver, and mercury, and precipitate the metals. Basic phosphites exist, in which the base is two or four times more in proportion than in the neutral salts.

9. *Hypophosphites* resemble the preceding, as respects the reaction of the phosphorus, from which they are distinguished by the circumstance of the phosphites being precipitated by lime or baryta water, which does not happen with the hypophosphites.

10. *Chlorates.* These detonate strongly when heated with charcoal, or any other combustible body; treated with hydrochloric acid, they disengage chlorine or its oxide. By calcination, they yield oxygen, and become transformed into metallic chlorurets.

11. *Chlorites* possess the taste and smell of chlorous acid; they bleach and destroy vegetable colours; hydrochloric acid disengages chlorine and its oxide.

They form basic salts, in which the proportion of base is doubled.

12. *Iodates* detonate feebly with combustible bodies, yielding oxygen by calcination, and leaving iodurets.

13. *Borates.* When decomposed by dilute and boiling sulphuric acid, they deposit, on cooling, crystalline plates of boric acid; when the acid liquor is evaporated to dryness, and the mass digested with alcohol, it acquires the property of burning with a green colour; when ignited on cotton soaked with the solution, the green colour is always very discernible, at least towards the termination, even when the quantity of boric acid is so small that it does not crystallize. Turner recommends the following process for ascertaining the presence of a minute portion of boric acid combined with other bodies. Fluor spar is pulverised, and in order to procure an exceedingly fine powder, the minuter portions are separated by water from those less comminuted: one part of this is taken and mixed completely with 4½ parts of dried bisulphate of potassa; this flux is mixed with an equal quantity of the substance for examination, which has been triturated; the mass is slightly moistened and placed in the ear of a thin curved platina wire, on which it is heated before the blow-pipe, so as to hold it in the point of the blue flame (that is to say, rather nearer the wick than the extremity of the blue flame). At the moment the mass fuses, it is surrounded by a beautiful green flame, if it contain boric acid; but this flame quickly disappears, and cannot again be produced with the same mass: it is therefore ne-

cessary to avail one's self of the moment of its appearance. By these means the presence of boric acid may be known with sufficient certainty, but we are wanting in reagents to separate it, when it exists in small quantity. Most of the borates are very fusible before the blow-pipe, and melt with a degree of swelling, owing to the disengagement of water.

Boric acid has such feeble affinities, and combines with bases in so many proportions, that it is difficult to say which of these combinations should be regarded as neutral; nevertheless, it is probable that borax (native borate of soda) is a neutral combination; and in this salt the capacity of the acid for saturation is one-sixth of its oxygen, or 11·468; other borates exist, in which the oxygen of the acid is to that of the base as 12, 6, 4, 3, and 2 are to 1.

14. *Carbonates* are dissolved by acids with effervescence, owing to the disengagement of carbonic acid; most of them lose their acid by calcination; others, when calcined to redness, after being mixed with powdered charcoal; in this case, carbonic oxide gas is disengaged. They form acid salts, in which there is 1½ and double the quantity of acid and basic salts, that contain two and four times more of base than those in which the oxygen of the acid is double that of the base.

15. *Oxalates* in solution are recognized by

the precipitate they form with the salts of lime, even when the liquor is slightly acid, and by their property of precipitating metallic gold from its solutions at the boiling temperature. In the solid and dry state, they decompose on calcination without becoming carbonised. Those bases that retain carbonic acid at a red heat (potassa, soda, baryta, strontia and lime), remain in the state of carbonates and disengage carbonic oxide gas; those bases which lose carbonic acid, but are not reduced (magnesia, the earths properly so called, the protoxides of manganese, of cerium and of chromium), remain in the state of oxides, whilst they disengage a mixture, in equal volumes, of carbonic acid and carbonic oxide gas; lastly, those bases which are easy of reduction leave a residue of metal, with the disengagement of carbonic acid; this is the case with most metals. Lead and zinc remain in the state of suboxides, and disengage carbonic acid and carbonic oxide.

The oxalates, with excess of acid, contain twice and four times as much of it as the neutral salts.

16. *Silicates.* Acids precipitate the silicic acid from them in the form of a semitransparent gelatinous mass. The alkaline silicates dissolve entirely in acid, and deposit silica during evaporation in the gelatinous form. The best method of discovering silica in the insoluble silicates, is to fuse them with three to four times their weight of car-

bonate of potassa; the fused mass is then treated with dilute hydrochloric acid: mixed with pure fluor spar and sulphuric acid, they yield on distillation the fluosilicic gas: this last is an examination which should be made in metallic vessels.

Before the blow-pipe, the silicic acid is discovered by fusing with phosphate of ammonia and soda; the silicic acid dissolves in very small quantity, whilst the greater part swims in the glass, in the form of a swollen mass, which, on cooling, produces the appearance of opal. Regarding as neutral the salts in which the silicic acid contains three times as much oxygen as the base, it forms acid salts that contain $1\frac{1}{3}$ and twice as much acid; and basic salts, in which the base is multiplied by $1\frac{1}{2}$, three and six.

17. *Acetates.* The best mode of discovering these salts, consists in mixing them in the dry state or in very concentrated solution, with sulphuric acid; the acetic acid that disengages is known by its peculiar smell. In the dry way, they are carbonized, yielding combustible gases and empyreumatic oil. No acid acetates are known: in the basic acetates, the base is multiplied by three and by six.

18. *Tartrates.* When mixed with bisulphate of potassa, they deposit after a time crystals of bitartrate of potassa. On adding a solution of

alum, or of a persalt of iron, to the solution of a tartrate, and adding an alkali to the liquor, no precipitate forms, when care has been taken to add less of the salt of alum or iron, than the presumed quantity of tartaric acid can hold in solution, for the alkali will precipitate the excess. In the dry way these salts are known by the characteristic odour disengaged by the tartaric acid, when it is decomposed at a high temperature.

In acid salts the tartaric acid is in double proportion; only one salt is known, with excess of base (tartrate of potassa and antimony), whose formation leads to the supposition that tartaric acid follows the same laws as the phosphoric in its basic salts.

19. *Citrates.* It is not easy to distinguish these from the reaction of their acid. They precipitate the neutral salts of lead, the same as most of the vegetable acids; when the precipitate is collected, and ammonia thrown on it, it dissolves; which property characterises the citrate of lead.

20. *Malates.* The soluble malates form a precipitate of malate of lead with the neutral nitrate of lead, which dissolves easily in boiling water, and crystallises on cooling in scales like mother of pearl. Malate of zinc dissolves also when warmed, and deposits in the form of needles on cooling. Malic acid, separated by sulphureted hydrogen

from the crystallised malate of lead, deposits in the form of irregular crystals, resembling the cauliflower in appearance.

21. *Benzoates.* This acid, but little soluble in water, is easily separated by hydrochloric and sulphuric acids; it precipitates in the form of needles, or of elastic plates unalterable by air, more soluble in alcohol than in water, and which, when heated, partly decompose whilst the remainder sublimes. Nitric acid dissolves them without alteration. The benzoates precipitate the persalts of iron of a brick colour. No acid benzoates are known. In those with excess of base, the latter is three or six times more in proportion than the acid.

22. *Gallates.* These darken the solutions of persalts of iron and transform them into ink: dissolved in water, they are quickly decomposed, becoming yellow, green, and finally brown; the base remains combined with carbonic acid, or with some other substance proceeding from the decomposition of the acid.

The gallates follow the same law as the benzoates in their different degrees of saturation.

23. *Mucates.* These are generally but little soluble: treated with hydrochloric acid, they give a deposit or residue of mucic acid, which is very slightly soluble in water.

The mucates when they are calcined give out an odour similar to that of the tartrates.

24. *Formates.* When the sulphuric acid is thrown on a formate, a smell of ants is perceived: mixed with nitrate of silver and gently heated, they reduce the silver; water, and carbonic acid, which disengages itself, then form.

The different degrees of saturation of the formates are like those of the acetates.

25. *Succinates* possess a smell like that of succinic acid. They precipitate the persalts of iron of a pale red colour. Hydrochloric acid easily separates the acid of these salts. Crystals of succinic acid, when heated, totally sublime, if pure, and dissolve more easily in warm than in cold water or alcohol.

The different degrees of saturation of the succinates are the same as those of the acetates.

36. *Cyanates.* Water and acids decompose them in such a way that they become transformed into carbonic acid and ammonia, without any trace of hydrocyanic acid.

27. *Fulminates*, when heated, occasion a violent and dangerous explosion. The oxygenated acids decompose them with a sensible disengagement of hydrocyanic acid.

28. *Seleniates.* These are easily known by the odour they exhale when heated before the blow-

pipe. Treated with sulphurous acid they yield selenium, which appears when cold of a red brick colour, and at a boiling temperature of a greyish black colour. Mixed in the solid form with sal ammoniac and heated in a distilling vessel, they disengage selenium reduced by the ammonia. When hydrochloric acid is added to them, and then sulphureted hydrogen, a yellow precipitate is obtained, which, on drying, assumes an orange colour.

In the acid salts there exist two and four times more acid than in the neutral salts; selenic acid has little tendency to form salts with excess of base, and their composition is not yet ascertained.

29. *Arseniates* are known by the smell they give out when heated with the blow-pipe in the reduction flame. Fused with boric acid and powdered charcoal in a glass tube closed at one end, they yield a sublimate of metallic arsenic. The presence of arsenic being established, the arsenic acid is distinguished from the arsenious by the brown precipitate that the nitrate of silver produces in the arseniates. They are also precipitated by lime water, like the phosphates. The deposit is examined before the blow-pipe. The insoluble arseniates, dissolved by nitric acid, yield a precipitate with acetate of lead, consisting of subarseniate of lead, which fuses before the blow-pipe and becomes reduced, occasioning a strong disen-

gagement of arsenical vapours. The arseniates supersaturated with a very weak acid, are difficultly decomposable by sulphureted hydrogen, and only after a prolonged action; the decomposition is easily effected when a concentrated solution is used. The precipitate is bright yellow.

They form acid and basic salts in the same proportion as the phosphates.

30. *Arsenites.* To discover the arsenic they are treated like the arseniates. They differ from them in this respect, viz., that nitrate of silver produces a bright yellow precipitate, especially when they are well saturated, and the liquor does not contain free acid. The arsenites treated with acid in excess give instantly, with sulphureted hydrogen, a beautiful yellow precipitate. They produce a green colour with copper, known by the name of Scheele's green; this reagent is not, however, certain. Heated in the solid state in distilling vessels, they often yield arsenious acid or metallic arsenic; in this latter case, an arseniate remains in the retort.

Their different degrees of saturation have not been sufficiently examined; but they appear to correspond to those of the phosphorous acid.*

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* When speaking of arsenious acid, M. Berzelius enters at great length on the means of establishing its presence in cases of poisoning. When the arsenious acid can be procured in the solid form from the stomach or intestines, he

31. *Chromates* are distinguished by their yellow, orange, or red colour. Before the blowpipe they colour the fluxes green, both in the reduction and oxidation flame. Mixed with me-

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recommends that it should be separated from the animal tissues by immersion and agitation in water, when the acid, from its greater specific gravity, will collect at the bottom of the vessel; and, on decanting the supernatant liquor, may be reduced to the metallic state by simply being heated to redness with charcoal (previously calcined by the blow-pipe, to deprive it entirely of moisture) in a narrow glass tube, which is drawn out at one end, so as to render it of still smaller diameter, and then sealed at the narrowest extremity, or in a tube like that represented in fig. 1.; he recommends that the tube be held horizontally in the lamp flame, and that the arsenic be not much heated until the charcoal (which is placed over the arsenic) be first brought to redness by holding it at the edge of the flame, whilst the arsenic being quite at the bottom of the tube, remains at first but slightly heated; the metallic arsenic will thus sublime and condense in the narrow part of the tube. He says that this plan succeeds on a portion of arsenious acid, so small that it is but just large enough to be carefully removed into the tube without being lost.

In cases where the poison exists in the stomach in the fluid state, Valentine Rose recommends that the matter be boiled in water, containing a few grains of caustic potassa, and then filtered; the filtered solution is again boiled, and whilst in this state nitric acid is added, so long as any precipitate appears, and until the liquor becomes clear and yellow; the boiling solution is now filtered, and nearly saturated with carbonate of potassa, care being taken to drive tallic chlorides and concentrated sulphuric acid, they disengage a red gas, with the aid of heat; which gives out smoke in the air and dissolves in water, colouring it yellow or red. Treated with

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away all carbonic acid. Lime water is then added, which combines with the excess of nitric acid, and precipitates with the arsenious acid, as arsenite of lime, but in a very impure state; this precipitate is washed on a filter and dried, and may be reduced by boric acid and charcoal, in the tube before mentioned.

M. Berzelius recommends that the liquor be boiled in an alkaline solution, which is to be afterwards saturated with hydrochloric acid, and filtered; this liquor may now be tested with sulphureted hydrogen, when, if arsenic be present, a yellow precipitate of sulphuret is produced, which is to be thrown upon a small quantity of fused nitre at the bottom of a tube; an arseniate of potassa is formed, which is dissolved in a little distilled water, and decomposed by a solution of lime, which precipitates arseniate of lime; it may be well to mention, that boiling much facilitates the formation of this precipitate. The test of reduction practised by M. Berzelius is performed with charcoal only, for though boric acid, when added, causes the sublimation to be produced at a much lower temperature, yet it swells so much by heat, that it should be avoided as much as possible in delicate operations. In using hydrochloric and sulphuric acids, care should be taken that they contain no arsenic, which is sometimes the case when they are prepared with arsenical pyrites; this source of fallacy is easily avoided by testing the acid reagents with a stream of sulphureted hydrogen.

The processes of Berzelius and Rose are in many points objectionable, and do not equal that proposed by Dr. Chrisalcohol and hydrochloric acid, they disengage ether, and become transformed into protochloruret of chromium, which colours the liquor green.

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tison, either in simplicity or accuracy; thus, the arseniate of lime is partly lost during the washings, being far from insoluble in water; and the arseniate, when heated with charcoal, even by the full red heat of a blow-pipe, only yields one third of its arsenic in the metallic state. Dr. Christison's process consists in boiling the mass in distilled water for half an hour, (which he has satisfactorily proved is capable of dissolving the arsenic present, provided the matter examined be previously cut into shreds): it is then filtered and acidulated with acetic acid, which precipitates the casein, &c.; the liquor is again filtered and treated with sulphureted hydrogen; the sulphuret is collected on a filter, and reduced with black flux, in a tube similar to that employed by Berzelius and Rose. Before treating the liquor with sulphureted hydrogen, it is well to see if the ammoniacal nitrate of silver give its characteristic yellow colour with the solution, which effect, if produced, will indicate that it is ready for the passage of the gas, but if it do not act satisfactorily, a necessity will be indicated for the further purification of the liquor, which may be effected by simply evaporating it to dryness, and boiling the residue with distilled water, when a liquor will be procured, which may be tested with the sulphureted hydrogen. As regards the quantity of sulphuret capable of giving satisfactory evidence of the presence of arsenic, I have produced a perfectly characteristic metallic crust from a portion of sulphuret not larger than half a grain of mustard seed; and this when freshly precipitated and dried, and therefore in a loose and uncondensed form.—*G. O. R.*

The acid chromates contain a double quantity of acid, and the basic chromates 1½ and twice the quantity of base contained in the neutral salts.

32. *Molybdates* possess a weak metallic taste. Acids produce in them a precipitate that dissolves in a greater excess of acid, nitric acid excepted. On placing zinc in the weak metallic solution it becomes first blue, then green, and becomes black and opaque, by the continued action of the zinc; lastly, the protoxide of molybdenum precipitates. If, instead of using zinc, the acid liquor be digested with copper, it becomes transparent and of a dark red colour: mixed, when dry, with sal ammoniac and heated, the molybdates yield a black mass, which treated with water leaves oxide of molybdenum, either alone, or in the state of metallic chloruret, mixed, if it be insoluble, with the base.

In the reduction flame of the blow-pipe they give a brown mass with the fluxes, and yield metallic molybdenum, when mixed with carbonate of soda, or else an alloy of this metal with the radical of the base, if this be reducible.

In the acid molybdates the quantity of acid is doubled.

33. *Tungstates.* These possess a bitter metallic taste. Acids precipitate the tungstic acid from them, which is insoluble in a greater excess of acid. If the acid mixture is digested with zinc,

they first become blue, then coppery red; the colouring matter is not, however, in solution: it is the oxide of tungsten, which, when the zinc is withdrawn, quickly passes to the state of acid. Mixed with the ammoniaco-phosphate of soda, and heated in the reduction flame of the blowpipe, these salts communicate a blue colour to the flux, unless the base of the salt be itself coloured; in this case it must first be separated by means of an acid. The blue colour becomes yellow in the oxidation flame, which distinguishes these salts from oxide of cobalt, which remains the same in the two flames. A little metallic tin reproduces the blue colour more easily than the reduction flame alone. If the tungstate contain iron, the glass obtained in the reduction flame will be red, and green if it contain tin. With carbonate of soda they yield (in the same flame) tungsten, or alloys of that metal.

They resemble the molybdates as regards their different degrees of saturation.

34. *Antimoniates and Antimonites.* Acids form precipitates with them, insoluble in an excess of acid. On passing a stream of sulphureted hydrogen through this mixture, the precipitate assumes an orange colour. Digested with the acid tartrate of potassa (supertartrate of potassa), and then with hydrochloric acid, whilst a piece of polished iron is placed in the mixture, the

antimony becomes reduced, and precipitates as a dark powder, easily known for antimony by the ease with which it fuses and burns. Tartaric acid troubles the solutions of antimoniates, but on the application of heat, the precipitate dissolves in a sufficient quantity of tartaric acid. There exists no other way of distinguishing the antimoniates from the antimonites than to separate the acid, and to try whether it disengage oxygen when heated. The metallic antimoniates are difficult to demonstrate. The acid must be extracted by a hydrosulphate (hydrosulphuret), and the sulphuret of antimony precipitated by hydrochloric acid.

35. *Tellurates* are all but little soluble. On charcoal they are reduced by the blow-pipe with the greatest ease, occasioning a detonation accompanied with a green flame. The best mode of establishing the presence of tellurium is by heating the matter for examination in a test tube with a little potassium; afterwards the mixture is placed in a small quantity of water, which, when it contains tellurium, assumes a red-wine colour, owing to the alloy of tellurium and potassium.

36. *Columbates.* Their acid is insoluble in hydrochloric acid, and the hydrosulphates (hydrosulphurets) produce no alteration in them. The silicates and titanates are similarly circumstanced; but the columbates differ from the first by the

milky colour of the acid, when it has been separated by stronger acids; by their weight, and by the property they possess of yielding, when heated by the blow-pipe with fused borax, a transparent glass, which becomes white on cooling, or when after being cooled it is again submitted to a gentle heat. They differ from the titanates, in as much as they do not colour the fluxes (columbic acid dissolved in the acid oxalate of potassa gives a yellow precipitate with the ferro-cyanuret of potassium: with the infusion of nut galls the liquor first becomes orange-yellow, and gives a precipitate of the same colour, on the addition of a greater quantity of the infusion).

Their different degrees of saturation are little known. In the native columbates with excess of base, the base is multiplied by 1½ and three.

37. *Titanates.* In the moist way they re-act like the preceding, but, mixed with the ammoniaco-phosphate of soda, and heated in the reduction flame of the blow-pipe, or by adding a little metallic tin to them, they produce a glass, whose colour is a beautiful purple approaching to blue, which becomes darker while cooling, and passes nearly to black when too much of the material has been used.

B. Haloide salts.*

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* A name used in distinguishing salts formed from non-oxygenated bases (from ἀλς salt, and ειδος resemblance).—*G. O. R.*

38. *Chlorurets* (or *chlorides*). In the moist way they are distinguished by giving with nitrate of silver a white precipitate insoluble in all acids, and very soluble in ammonia. Heated with concentrated sulphuric acid and peroxide of manganese, they disengage chlorine. Before the blow-pipe they are recognised, by first fusing some ammoniaco-phosphate of soda with the black oxide (peroxide) of copper nearly to the saturation of the free phosphoric acid, and then adding a little of the salt for examination; chloruret of copper then disengages itself, which for some moments gives a blue colour to the flame which surrounds the little glass bead.

Few acid chlorurets are known; but some exist with excess of base formed by the chloruret and the oxide of the same metal; the oxide then contains 1, 2, 3, and 4 times as much metal as the chloruret.

39. *Iodurets.* In a dissolved state they give a deposit of iodine by the action of a solution of chlorine or of nitric acid, easily known by the colour and smell which the liquor assumes. When the iodine is in small quantity, the best mode of discovering it is to mix it with starch, to which it communicates a colour that varies according to the proportions of iodine and starch, which may be red, brown, black, or blue. When the iodurets are mixed with chlorurets the examination is

differently conducted, especially when the quantity of iodine is small, since, on adding the nitric acid, the chloriodic acid forms, which does not colour the starch. In this case the starch is dissolved in a little weak boiling sulphuric acid; the solution is mixed with the liquor for examination, some drops of a solution of chlorine are added, and the mixture is shaken.

If the solution be too dilute, the re-action may be imperceptible. Before the blow-pipe the iodurets are recognised by a test similar to that which I have recommended for the chlorurets; at the moment when the ioduret is added to the flux, the flame assumes a beautiful green colour.

40. *Fluorides.* These salts, when mixed with sulphuric acid, act upon glass. When they are in solution, sulphuric acid is added to them, and the mixture is thrown on a plate of glass, the surface of which is covered with a coat of wax, on which a drawing has been made so as to expose some portions of the surface of the glass. The liquor is left to dry on it.

When only very small quantities of the substance are used, or else a compound containing but little fluoride, or which is silicious, the solution is evaporated on a watch glass; this however must be made of glass that is unacted on by other acids: afterwards, on dissolving the salt, the glass is seen to be affected in those places where the saline mass remained during the desiccation. It is always best to employ the matter for examination in the solid form: when it contains silica the following process must be employed, which is, besides, a very good mode of discovering the least trace of fluorine in a mineral. The material is placed in a glass tube eight or ten inches long, and open at both ends: it is fixed near to one of the openings of the tube, or else on a small piece of platina foil in the form of a half circle, which is introduced into this glass tube: this extremity of the tube is then inclined downwards, and heated to redness with the blow-pipe: the flame is directed into the tube, so that the products of the calcination are driven through it. The heat now disengages fluosilicic acid, which condenses in the interior of the tube with the water formed by the flame, and deposits silicic acid, which, after being heated to evaporate the water, remains in the form of rings the size of drops.

The colourless fluorides, when placed in water, refract the light nearly to the same extent as this liquid, so that they disappear in it in some degree. Their neutral solutions, even those of potassium and sodium, cannot be either evaporated or preserved in glass vessels without acting on them. Some fluorides form acid salts by combining with hydrofluoric acid; and by uniting with the oxide of their metal (or base) they give rise to salts with excess of base, in which there are 1, 2, 3, and 4 times as much metal as in the fluoride.

41. *Borofluorides* (*fluoborates*). Distilled when dry, they yield fluoboric gas and a residue of metallic fluoride. Distilled with sulphuric acid they yield a portion of liquid hydrofluoboric acid, besides this gas.

Their composition is such that the electro-positive metal contains four times more fluorine than the fluoride, and half as much boron as the neutral oxy-salt.

42. *Silicofluorides* (*fluosilicates*). Heated when dry, they yield fluosilicic gas, leaving a residue of metallic fluoride. Heated with sulphuric acid, they disengage a great quantity of fluosilicic gas. The alkalies separate from their solutions either the silicic acid alone (in these cases the salts are with alkaline bases), or a metallic fluoride united to the silicic acid (salts with alkaline earths for bases), or a silicate of the oxide (salts with earths or metallic oxides for base).

In these salts, the electro-positive metal contains three times more fluorine than the fluoride, and the quantity of silicium necessary to form an oxy-salt, in which the silicic acid contains twice as much oxygen as the base.

43. *Cyanurets.* They give a dark blue precipitate with the salts of iron (Prussian blue), or

a white precipitate which becomes blue by contact with air, even when the liquor contains a great excess of acid.

44. *Sulpho-cyanurets* are as easy to distinguish as the preceding, for they occasion an intense red colour with the persalts of iron, but an excess of acid destroys it. This red colour is also produced by some vegetable acids, such as the meconic, and by some combinations but little known of chlorine and iodine with fulminic acid.

(C) *Sulpho-salts.* A small number only of these salts are as yet known.

The following is a mode of preparing them, which deserves to be added to those methods already shown, to which I refer.* A stream of sulphu-

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* These methods are as follows:—

a. The sulphuret of potassium dissolved in water is mixed with the electro-negative sulphuret, which dissolves to the saturation of the sulphuret of potassium: this salt is then used to transform an oxy-salt, which contains another base, into a sulpho-salt, by double decomposition.

b. The hydrosulphate of the sulphuret (hydrogureted sulphuret) of potassium is mixed with the electro-negative sulphuret, which dissolves with effervescence driving off the sulphureted hydrogen, as a stronger acid drives away the carbonic.

c. The electro-negative sulphuret is dissolved in caustic potassa: the metal then passes to the state of acid at the expense of the potassa, and combines with another portion of potassa to form a metallic acid salt: the reduced potassium unites with the sulphur which is separated from the reted hydrogen is passed through the neutral solution of an oxy-salt so long as absorption takes place, and with certain salts; for instance, the tellurets and the seleniates, until a precipitate

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electro-negative metal, and the sulphuret of potassium enters into combination with the non-decomposed metallic sulphuret. It is thus that the sulphuret of arsenic dissolves in potassa, with the formation of sulphuret of potassium, and arsenite of potassa.

d. When a solution of hydrosulphate of sulphuret of potassium is mixed with a metallic acid, this last transforms itself into a metallic sulphuret at the expense of the sulphureted hydrogen; but as the metallic sulphuret so formed is not sufficient for the saturation of the sulphuret of potassium, a portion of this last is decomposed: the potassium passes to the state of potassa by means of the oxygen of the metallic acid, and the electro-negative metal unites with the sulphur of that portion of potassium to which it has yielded its oxygen. The potassa formed combines with part of the metallic acid, so that in this case a sulpho-salt and an oxy-salt are formed at the same time. When the experiment is made with the hydrosulphate of sulphuret of ammonium (hydrosulphuret of ammonia) and arsenious acid, or the hydrated oxide of tin, an alkali is set at liberty; for the affinity of ammonia for oxide of tin or arsenious acid is too weak to enable it to form a salt with these bodies. It is on this account that the solution gives out an ammoniacal odour a short time after the mixture is made. The hydrosulphates of the alkaline sulphurets are frequently used in analysis to separate the greater number of electro-negative metallic oxides that they can dissolve, from the electro-positive oxides, which can be transformed into sulforms, which no longer dissolves when the liquor is shaken.

If this point be exceeded, the sulphureted hydrogen will precipitate the metallic sulphuret, and take its place. This process does not succeed well, except for salts with metallic acids. The hydrosulphate of the sulphuret of ammonia* may be used instead of the sulphureted hydrogen, when the oxy-salt has an alkaline base: the ammonia that then becomes free, and the excess of the ammoniacal salt, are dissipated by distillation.

By this mode of preparation, sulpho-salts are obtained, in which the radicals of the acid and the base are combined with sulphur, in volumes equal to those of the oxygen which they have lost, so that the sulphur of one of the sulphureted bodies is always a multiple (by a whole number) of the sulphur of the second.

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phurets, but without being dissolved in the alkaline sulphuret.

e. Lastly, these combinations can be obtained in the dry way; for instance, by mixing the electro-negative sulphuret with an alkaline carbonate in proper proportion, and calcining in closed vessels. The carbonic acid is driven off, and the alkali acts on the sulphuret as in the moist way, so that an oxy-salt with a metallic acid and a sulpho-salt are obtained at the same time. This latter can generally be separated from the former by solution and crystallisation.

* Hydrogureted sulphuret of ammonia.

45. *Sulphohydrates* (hydrogureted sulphurets). When speaking of sulphureted hydrogen, I remarked that it transformed the alkalies, the earths, and the oxides of other metals into sulphurets, that is to say, into bases of sulpho-salts. Sulphureted hydrogen produces salts soluble in water, with eight of these bases, (those formed by the alkaline sulphurets of potassium, sodium, lithium, and ammonium*, and by the sulphurets of the alkaline earths, barium, strontium, calcium, and magnesium,) possessing a very disagreeable hepatic smell. This odour is not peculiar to the salt itself, but it is a consequence of its continual decomposition by the carbonic acid of the atmosphere, which disengages the sulphureted hydrogen.

Those salts which have the sulphurets of potassium, sodium, and lithium for their base can be calcined to redness, in closed vessels, without losing their sulphureted hydrogen. The sulphohydrate (hydrogureted sulphuret) of ammonium is volatile, and the others are decomposed by heat. The salts of magnesium and of calcium cannot even be obtained but in a state of solution.

To distinguish a sulphohydrate from a sulphureted base, the effervescence, owing to the escape of sulphureted hydrogen, on the addition of an acid, cannot be considered as a sign; for, even as regards quantity, this phenomenon is nearly the same in these two kinds of compounds. The best mode of ascertaining whether a sulpho-salt be operated on is that of adding a neutral and concentrated solution of a salt with oxide of zinc, protoxide of manganese, or protoxide of iron for a base. A metallic sulphuret then forms without the disengagement of sulphureted hydrogen, when the solution of a sulphureted base is operated on; whilst there is at the same time a disengagement of sulphureted hydrogen when it is a sulphohydrate.

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* Ammonia is called ammonium by Berzelius, not with the idea that it is a metal, but merely because it resembles metals in some of its re-actions.

The sulphohydrates are decomposed by air: if the contact of air be slight, the sulphureted hydrogen alone is decomposed, and a metallic sulphuret is obtained which is a little soluble, and deposits in the form of yellow crystals when there is lithium, or an alkaline earth for the radical.

If, on the contrary, free access of air be allowed, part of the sulphuret also oxidises and transforms itself into hyposulphate, whilst part passes to a higher degree of sulphuration. It is for this reason that the sulphohydrates, though colourless themselves, become yellow almost instantly when the contact of air is allowed.

The sulphohydrates are decomposed by all the oxygenated bases: these last are then reduced to the state of sulphurets by the sulphureted hydrogen, and at the same time a weaker oxygenated base exchanges its oxygen with the sulphur of the stronger base, so that, for instance, if oxide of copper or zinc be placed in a solution of the sulphohydrate of potassium, water, sulphuret of copper or of zinc, and potassa, are formed.

In these salts the sulphur of the base is equal to that of the acid; no other degrees of saturation are known.

46. *Sulphocarbonates.*[*] It is difficult to obtain these perfectly pure, both because the sulphuret of carbon does not decompose the sulphureted bases that possess a higher degree of sulphuration, and consequently remain mixed, and because the oxygenated salifiable bases are only decomposed with difficulty by them, with the formation of an oxycarbonate and a sulphocarbonate. The best means of obtaining them consists in digesting a mixture of sulphuret of carbon, water, and an alkaline sulphuret, (such as the sulphurets of potassium, sodium, and calcium,) in a closed vessel at a temperature of 30°.[†] The combination is not completely finished till after the lapse of many days.

Solutions of liver of sulphur in alcohol mixed with sulphuret of carbon yield sulphocarbonates; but they precipitate the sulphur very imperfectly from the hepatic solutions of alkalies in alcohol, and they do not precipitate it from the solutions of alkaline earths. Water separates the sulphuret of carbom from them and leaves the hepar, or a mixture of sulphocarbonate and of sulphur in excess.

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[*] Combinations of the sulphuret of carbon.

[†] Equal to 86° of Fahrenheit. — *G. O. R.*

The sulphocarbonates with alkaline radicals have a darker colour than the sulphurets: their taste is at first cool, then warm and biting, with an hepatic taste afterwards. Calcined in closed vessels they are entirely decomposed. Those with alkaline bases fuse and yield sulphurets becoming more highly sulphureted on depositing carbon, which may be separated by treatment with water, which dissolves a sulphuret containing three times as much sulphur as the sulphureted base. The sulphocarbonates of alkaline earths and metals, when heated, yield a residue of sulphuret, and disengage sulphuret of carbon.

When the salt contains water the phenomenon is often complicated, owing to the decomposition of this liquid, but it is always easy to account for it. The sulphocarbonates, when dry, or in a concentrated solution, do not undergo any alteration, and may be preserved a long time. When a sulphocarbonate contains a sulphuret that can form salts at a still higher degree of sulphuration, such as the sulphocarbonate of iron, bearing proportion to the protoxide of iron, it absorbs the oxygen of the air during desiccation, and transforms itself into a mixture, perhaps a combination, of hydrated oxide and of sulphocarbonate at a higher degree of sulphuration, which is permanent. The sulphocarbonates of the four alkalies, and the four alkaline earths, are all soluble in water; the others are insoluble, but dissolve in the former in greater or less quantity. When a soluble sulphocarbonate is mixed with hydrochloric acid an oleaginous matter is formed, composed of sulphuret of carbon and sulphureted hydrogen, which displays acid properties, as M. Zeise, who first separated it, has shown: the liquor at first assumes a yellow, milky appearance, and some time elapses before the oily substance collects. The less energetic oxygenated bases decompose these salts, so as to transform the weaker radical into a sulphocarbonate, while the stronger oxidises at its expense. Their dilute solutions are quickly decomposed by the air: when made to boil with the exclusion of air, the water is decomposed, and they transform themselves into carbonates with a disengagement of sulphureted hydrogen.

The neutral salts are so composed that, if the sulphur be replaced by proportional quantities of oxygen, carbonates are produced.

47. *Hydrosulpho-cyanates.* These salts result from the combination of electro-positive sulphurets with an electro-negative compound of

sulphur, known by the names of hydrosulphocyanic acid: almost all these salts have a more or less dark lemon colour.

They are known by the properties they possess of forming a yellow precipitate with the salts of copper, and a bright yellow precipitate with the salts of mercury and lead, which passes quickly to black: such of these salts as are soluble transform themselves (when exposed to the air, in solution) into metallic sulphocyanurets, whilst the hydrogen forms water with the oxygen of the air, and the sulphur of the base deposits in a crystalline form. When treated with a metallic oxide their hydrogen is neutralised at the expense of this oxide, the sulphur unites to the reduced metal, and the liquor only contains a metallic sulphocyanuret, as when the oxygen is furnished by the air. These salts are decomposed by ebullition: a temperature of 50°* (centigrade) suffices to commence their decomposition with disengagement of sulphureted hydrogen, and a deposit of a yellow powder which appears to be hydrosulphocyanic acid. Distilled they yield no oxygenated products, which proves that oxygen does not enter into their composition. The constituent proportions of these salts are such, that when the hydrogen of the acid unites with the sulphur of the base to form sulphureted hydrogen, a metallic sulphocyanuret remains.

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* Equal to 122° of Fahrenheit.

48. *Sulpho-arseniates.* In these salts the degree of sulphuration of the arsenic is proportional to the composition of the arsenic acid. The alkaline sulpho-arseniates have, when dry, a lemon yellow colour, and are colourless, or slightly yellowish, when they contain combined water. Their taste is hepatic, nauseous, and bitter. Decomposed by an acid they give out an hepatic smell, similar to that of the orpiment in linseed oil varnish. When the solutions are concentrated, or the salts are dry, sulphureted hydrogen is at the same sime disengaged, which does not happen so as to be visible in dilute solutions. The sulpho-arseniates, formed by the radicals of alkalies, of alkaline earths, of glucina, and of yttria, and a few of the metals are alone soluble in water. They have a great tendency to form salts with excess of base that generally crystallise, which seldom happens with neutral salts. Some amongst them can combine with an excess of electro-negative substances, but on treating them with water the supersaturation is not complete; and besides, the concentration and temperature exercise a great influence on them. A solution that has been boiled with an excess of electro-negative sulphuret partly deposits it on cooling. Alcohol decomposes the neutral solutions of these salts in

such a manner as to form a salt with excess of base, whilst the liquor retains a salt containing twice as much sulphuret of arsenic.

By dry distillation the neutral salts yield sulphur, and transform themselves into sulpho-arsenites: the salts with excess of base do not undergo any alteration. The salts with alkaline radicals, even those of barium, resist an incipient white heat: all the others abandon the sulphuret of arsenic more or less completely, leaving as a residue the sulphur which served them for a base. Heated with contact of air they decompose very easily: the base passes to the state of oxide or of sulphate; that of the metallic sulpho-arseniates sometimes transforms itself into an arseniate.

In the dissolved state, the metallic oxides decompose them, so that an arseniate of the oxide remains in the solution, whilst a sulpho-arseniate, with excess of electro-positive sulphuret, deposits. When the solutions are concentrated, these salts keep well in the air; but in weak solutions they decompose, though very slowly: it requires many months to complete the decomposition. The liquor becomes troubled; it deposits sulphuret of arsenic and sulphur; the undecomposed portion of the salt remains dissolved with the arsenite and hyposulphite, which, when the decomposition is completed, becomes transformed into sulphate. The sulpho-arseniates form double salts with ease:

when the oxy-salts combine as double salts, the corresponding sulpho-arseniates also unite. The alkaline sulpho-arseniates besides dissolve a great part of the metallic sulpho-arseniates. In the sulpho-arseniates, whose different degrees of saturation have been remarked, the sulphur of the sulphuret of arsenic is to that of the base as 5 to 1, 2, and 3, admitting that the relation of neutral combinations is, as in the oxy-salts, as 5 to 2.

49. *Sulpho-arsenites.* These salts contain orpiment, or the sulphuret of arsenic corresponding to the arsenious acid. They cannot be obtained in the solid and neutral form, but in the dry way; for their solutions are decomposed at a certain degree of concentration, occasioning a brown pulverulent deposit, which is a hyposulpho-arsenite, whilst the liquor contains a sulpho-arseniate with excess of base: the decomposition does not, however, become complete until this latter crystallises.

On diluting the solution, and boiling it, the deposited matter is re-dissolved, and the sulpho-arsenite is reproduced. The decomposition takes place likewise in the dry way, when the prepared salts are treated with water, or when alcohol is added to a weak solution of sulpho-arsenite: this liquid precipitates a salt with excess of base, which soon becomes black, owing to the decomposition I have just mentioned. When alcohol is thrown into the solutions of basic, sulpho-arsenites of ammonium, of barium, or calcium, this decomposition of the precipitated basic salt does not take place, except when the solution contains a neutral salt, or one with excess of orpiment. When orpiment is dissolved at the ordinary temperatue, and to perfect saturation, in a weak solution of caustic potassa, or in the hydrosulphate of the sulphuret of potassium, a salt is obtained that contains twice as much orpiment as the neutral salt. On digesting this salt with orpiment prepared in the moist way, this latter is transformed into realgar; and the solution deposits arsenic passing from sulpho-arsenite to sulpho-arseniate.

The alkaline sulpho-arsenites resist heat: the sulphureted base can retain at a red heat many times the quantity of orpiment necessary for its equable saturation.

The other salts are decomposed by a red heat: orpiment distils from them, and a salt remains with excess of base, or the sulphureted base alone. In other respects the sulpho-arsenites act like the sulpho-arseniates as to metallic oxides and the acids, when under the influence of air and an open fire.

In their various degrees of saturation the sulphur of the sulphuret of arsenic is to that of the base, as three is to 1, 2, and 3; the neutral combination being in the proportion of 3 to 2.

50. *Hyposulpho-arsenites.* These salts contain

the red sulphuret of arsenic or realgar, to which no known combination of oxygen and arsenic corresponds. They are obtained in the dry way by fusing sulphureted bases with realgar, or sulpho-arsenites with arsenic; but they then retain so much realgar that the fused mass no longer dissolves in water: the neutral combination obtained in the dry way is decomposed by water, gives a black or dark brown deposit of sulphuret of arsenic, and transforms itself into a sulpho-arseniate. These salts cannot be obtained by the immediate combination of realgar with a caustic alkali, or with a hydrosulphate (hydrosulphuret); for a sulpho-arseniate and dark sulphuret of arsenic form as before. They may be obtained by dissolving orpiment at a boiling heat, in a concentrated solution of carbonate of potassa or soda, and filtering the clear boiling liquor: it becomes opaque on cooling, and deposits a number of brown flocculi resembling kermes mineral: this is a neutral combination of alkaline sulphuret with the realgar. They can also be obtained by evaporating sulpho-arsenites so as to make the solution crystallise: these salts are red or dark brown; most of them are insoluble in water. Those with an alkaline base are transformed by pure water into soluble salts with excess of base, and into insoluble salts with excess of realgar. The acids also precipitate realgar from them.

51. *Sulpho-molybdates.* These salts contain the sulphuret of molybdenum, which in its composition bears relation to the molybdic acid. Those with alkaline or earthy bases are soluble in water: in the neutral state the solution is of a beautiful red colour; it inclines to brown when it has an excess of sulphuret of molybdenum, and to yellow when it contains an excess of sulphureted base. These salts crystallise; and the crystals are brown or ruby coloured, seen by transmitted light, and a beautiful green by reflected light. The acids decompose them, and precipitate the sulphuret of molybdenum, when added in excess, in the form of a brown powder almost black; sulphureted hydrogen is disengaged at the same time. By dry distillation they decompose: the sulphureted base combines with part of the sulphur of the sulphuret of molybdenum. On the addition of water this persulphuret is decomposed, and grey sulphuret of molybdenum remains; or else when the base cannot pass to a higher degree of sulphuration sulphur is disengaged, and the residue contains either a combination or a mixture of the grey sulphuret of molybdenum with the sulphureted base. The sulphuret of molybdenum corresponding to the molybdic acid reciprocally does not decompose the higher degrees of sulphuration of the alkaline metals, and alkaline earths in the moist way. The neutral concentrated solutions

keep well exposed to the air; but they are quickly decomposed when they possess an excess of sulphureted or oxygenated base. The weak solution becomes by degrees brown when exposed to air: the base partially oxidises and passes to the state of hyposulphite, whilst a sulpho-salt with excess of sulphuret of molybdenum forms in the solution. This latter is finally decomposed; sulphuret of molybdenum deposits, the solution becomes blue, and now contains the base in the state of oxide, combined either with one of the acids of sulphur, or with the molybdic acid; the blue colour is owing to the molybdate of molybdenum.

This decomposition, however, proceeds so slowly that the solution drys, and the salt must be redissolved many times before it is completed.

The sulpho-molybdates form many degrees of saturation. In those that are neutral the sulphur of the sulphuret of molybdenum is to that of the base as three to one.

52. *Hypersulpho-molybdates.* These salts contain the molybdenum at a higher degree of sulphuration, possessing twice as much sulphur as the grey sulphuret of molybdenum. There exists no oxygenated combination that corresponds to this sulphuret. These salts are all yellow or red, pulverulent, and rarely crystallised. They are insoluble in water, except those with alkaline bases, which, however, only dissolve in

boiling water, but without depositing while cooling. The solution is dark red. Acids precipitate flocculi of sulphuret of molybdenum, of a beautiful dark red colour, from these salts; sulphureted hydrogen being disengaged at the same time. There exist, also, sulpho-phosphates, sulpho-seleniates, sulpho-antimoniates, sulpho-tungstates, and sulpho-stannates, but they are not yet well known.

RULES FOR OBTAINING A KNOWLEDGE OF SALTS FROM THE RE-ACTION OF THEIR BASES.

1. *Salts of potassium.* They are all very soluble, with few exceptions: many of them become moist in the air. In the solid state they do not contain water of crystallisation so frequently as other salts. They support a red heat better than other salts; so that the acids which, united to other bases, are dissipated or decomposed by heat, are preserved when united to potassa. In order to ascertain the presence of potassa in a salt the tartaric acid is employed, a concentrated solution of it being mixed with a concentrated solution of a salt of potassa; a deposit of bitartarate of potassa then forms, either immediately or after waiting a short time. Potassa may also be known by means of a saturated solution of sulphate of alumina, which precipitates alum: this last deposits,

after some time, in a crystalline form (the ammoniacal salts also possess this property). Lastly, chloride of platinum is used, which forms an almost insoluble double salt with the salt of potassa, which precipitates immediately, or deposits, during evaporation, in the form of little brilliant yellow crystals; the same thing again occurs with the ammoniacal salts, so that the examination should always be made with salts previously calcined.

2. *Salts of sodium.* They are colourless like those of potassa, which they likewise resemble in taste, and sometimes, also, in crystalline form. No characteristic sign is known for the detection of soda in these salts; but its presence is admitted when the re-actions that characterise potassa, ammonia, and lithia are wanting, and when the solution of the salt does not precipitate by carbonate of potassa. To demonstrate soda in a positive way, it must be separated from the acid with which it is united, and combined with sulphuric or phosphoric acid, or generally with any acid with which it forms well characterised salts.

3. *Salts of lithium.* These are distinguished by the property this alkali possesses of forming a salt of difficult solution with phosphoric acid. A saline solution contains lithia, if, when cold, it be not precipitated by a caustic alkali, nor,

when warm, with an alkaline carbonate; and if mixed with phosphate of soda it becomes turbid while evaporating, and leaves a white powder when it is treated with water, after being dried. The salts with a base of lithia are generally very fusible, and communicate this property to other salts. An alcoholic solution of a salt of lithia burns with a purple flame.

4. *Ammoniacal salts.* Mixed with the alkalies, or the hydrated alkaline earths, they disengage ammonia, which, when it is too small in quantity to be sensible to the smell, may be known by the smoke it forms when a tube, dipped in acetic, nitric, or hydrochloric acid, is held over the mixture. All the neutral ammoniacal salts contain combined water, a portion of which seems necessary for their existence (the anhydrous ammoniacal salts are always with excess of base): they have a sharp saline taste. Many of them volatilise without decomposition; others disengage ammonia at a higher temperature, deserting their acid; but most of them are decomposed in such a manner that the hydrogen of the ammonia reduces the acid to a less degree of oxidation, or entirely destroys it, with a disengagement of water and azote. Many ammoniacal salts lose ammonia when their solutions are evaporated, and pass to the state of acid salts; it follows, therefore, that when they are evaporated for crystallisation am-

monia must be added to them when the evaporation is finished.

5. *Salts of Barium.* These possess a disagreeable saline bitter taste, and form a white precipitate with sulphuric acid and the sulphates, which is insoluble in the hydrochloric and nitric acids.

6. *Salts of Strontium* are distinguished by the property of communicating a red colour to the flame of burning substances. Thus, the alcoholic solution of a salt of strontia also burns with a beautiful red colour. They are precipitated by sulphuric acid, like the salts of baryta; but they differ from them in not being precipitated by the hydrofluosilicic acid.

7. *Salts of Calcium.* These possess a bitter and sharp taste, similar to that of the salts of baryta. The presence of lime is established by the oxalic acid, which precipitates it, even when the solutions are very dilute. In those that are concentrated, it may be detected by sulphuric acid, which forms a very voluminous precipitate of gypsum. The salts of lime, soluble in alcohol, colour the edges of the flame red, as if it contained a salt of strontia in mixture. (The chloride of calcium is an extremely deliquescent salt.)

8. *Salts of Magnesium.* These have a very disagreeable bitter taste, which is peculiar to them The bicarbonated alkalies do not precipitate them, and the carbonates but incompletely, at the ordi-

nary temperature. The neutral salts of magnesia are partially precipitated by ammonia: weak solutions, to which a little acid, or a small quantity of ammoniacal salt, has been added, are not precipitated by ammonia, unless a great excess of it be added. The surest reagent for magnesia is the phosphate of ammonia with excess of base, such as we have already spoken of. The magnesian salts, mixed with a little nitrate of cobalt, and heated to redness by the blow-pipe, become of a light rose colour when they contain no other base.

9. *Salts of Aluminum* have a tart, astringent, and rather sweet taste; they are precipitated by the alkalies, but an excess of potassa or soda redissolves the precipitate. A saturated solution of sulphate of potassa, added to a somewhat concentrated solution of a salt of alumina, produces a white powder, which is alum. The dried salts of alumina, mixed with a little nitrate of cobalt, and strongly calcined by the blow-pipe, assume a beautiful azure blue colour: this reaction is altered by the presence of another metallic oxide.

10. *Salts of Glucinum.* These are characterised by a sweet and astringent taste. The alkalies precipitate them; but potassa or soda, when caustic or in the state of carbonates, redissolve the precipitate: the carbonates dissolve it in less proportion, however, than the alkalies.

(Ammonia does not dissolve it; but the carbonate of ammonia dissolves it easily.) The ferrocyanuret of potassium does not precipitate these salts, but the hydrosulphate of sulphuret of potassium (hydrogureted sulphuret of potassium) precipitates them, disengaging sulphureted hydrogen. A characteristic property of the salts of glucinum is, that when a warm solution of one of these salts is mixed with a warm solution of fluoride of potassium until a precipitate is perceived, and the mixture left to cool, little scales are deposited of a double salt, that is but little soluble.

11. *Salts of Yttrium.* These have a saccharine and astringent taste like the preceding; their density is greater than that of other earthy salts. Some of those that are crystallised have a red amethyst tint, which is very probably owing to the presence of manganese.

The ferrocyanuret of potassium forms a white precipitate; potassa acts in the same way, — an excess of which does not redissolve the precipitate. A very great excess of alkaline carbonate, and especially of carbonate of ammonia, redissolves the precipitate; but only in small quantity, relatively to the quantity of solvent required. The most positive character of yttria is that of forming an easily crystallisable salt with sulphuric acid, which is efflorescent at a temperature of

40°*, and becomes milk-white without losing its crystalline form: it is distinguished, moreover, by the extreme difficulty with which it dissolves; so that it is at first regarded as insoluble, although it by degrees entirely dissolves. The saturated solution contains from 1-45th to 1-30th of its weight of the salt.

12. *Salts of Zirconium.* The salts of zirconium have a purely astringent taste. The sulphate of potassa precipitates them, for this salt takes part of their acid in order to pass to the state of acid sulphate. Caustic potassa precipitates them; but an excess of the precipitant does not redissolve the precipitate. (The carbonates of potassa and soda do not dissolve hydrated zirconia; but when a salt of zirconia is precipitated by an alkaline carbonate in excess, the precipitate is redissolved: which is best seen by allowing a solution of zirconium to fall *guttatim* into a solution of an alkaline carbonate, and shaking the liquor.) The cyanuret of mercury and the ferrocyanuret of potassium do not precipitate these salts. The hydrosulphate of sulphuret of potassium precipitates the hydrated earth with a disengagement of sulphureted hydrogen. The infusion of galls precipitates them of a yellow colour.

13. *Salts of Cerium.*

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* Equal to 104° of Fahrenheit.—*G. O. R.*

(*a*) *Salts of the protoxide.* These are colourless; some, however, have a light red amethyst colour, similar to the shade of the salts of manganese; their taste is at first saccharine, then astringent. They are so analogous to the salts of yttria, that they cannot be distinguished from these latter but by their property of forming a double salt with sulphate of potassa, which salt is insoluble in a saturated solution of the sulphate of that base. The ferrocyanuret of potassium forms a white precipitate; sulphureted hydrogen does not alter them, but the hydro-sulphates precipitate them with the disengagement of sulphureted hydrogen. It is generally difficult to obtain them free from the deutoxide.

(*b*) *Salts of the deutoxide.* These are obtained by dissolving the calcined oxide in the acids. They have a yellow colour, sometimes orange yellow; a sweet, tart, and strongly astringent taste. They disengage chlorine when boiled with hydrochloric acid, and are reduced to the state of protosalts. The hydrosulphates form white precipitates.

14. *Salts of Manganese.*

(*a*) *Salts of the protoxide.* They generally form colourless solutions with water; sometimes the liquor is of a light rose colour: their taste is bitter and astringent. The caustic alkalies precipitate them white; the precipitate becomes yellowish when exposed to the air, then reddish brown, and lastly black. The alkaline carbonates also form white precipitates, which, when left exposed to the air, assume a light rose colour after a certain time. When these salts are neutral, the ammonia precipitates half the protoxide from them, and forms a double salt with the other half, in which the ammonia and the protoxide saturate equal quantities of acid. If the solutions are sufficiently acid to form a double salt with the ammonia, no precipitation takes place, whatever may be the quantity of ammonia afterwards added. The solution that contains an excess of ammonia is decomposed by degrees in the open air, and deposits the hydrated oxide. The solutions of the protoxide of manganese are not precipitated either by tincture of galls or by the alkaline chromates; nevertheless, the chromates form a brown precipitate after some time, owing to the reduction of the chromic acid. The hydrosulphates form brick coloured precipitates; and the ferrocyanuret of potassium a white precipitate, which by degrees becomes red. (The protoxide of manganese, precipitated from a solution that contains silicic acid, attracts this last; so that, in analysis, the silica must first be separated by dissolving the precipitate in hydrochloric acid and evaporating to dryness.)

(*b*) *Salts of the peroxide.* These have been but little examined, for they very easily transform themselves into oxygen (which disengages itself) and into protosalts. Their colour is dark violet, verging on red; and sometimes black, approaching to yellow or red. The combustible bodies, when digested in them, easily transform them into protosalts.

15. *Salts of Iron.*

(*a*) *Salts of the protoxide.* These have a bluish colour, which sometimes approaches to green; and a peculiar taste, at first sweet, and then astringent. Nearly all of them dissolve in water; the solution absorbs the deutoxide of azote, and assumes a dark brown or black colour. In closed vessels, the tincture of galls does not alter them: the ferrocyanuret of potassium precipitates them of a white colour: exposed to the air they become turbid, and deposit an ochre coloured powder, which is a basic salt of the peroxide; they at the same time assume a green or yellow colour, and become transformed into double salts with bases of protoxide and peroxide. (They likewise possess, in common with the salts of manganese and of magnesia, the property of being only partly precipitated by ammonia.)

(*b*) *Salts of the peroxide.* These have a yellow or red colour; an acrid, astringent, and slightly sweet taste. Most of these salts are soluble in water, and some have a great tendency to form basic salts, so that the alkalies do not entirely decompose them. The ferrocyanuret of potassium produces a beautiful dark blue precipitate with them, and gall-nut a black precipitate. In the neutral state, solutions of these salts have a dark brown red colour, which disappears by an excess of acid, and becomes bright yellow. The alkalies precipitate then completely, of a brownish red colour; those that are neutral decompose when boiled with water; a salt with excess of base deposits, and the solution retains a great excess of acid.

16. *Salts of Cobalt.* These salts possess a red or dark red colour. Those that are soluble have an astringent and rather metallic taste: hydrosulphate of potassa forms a black precipitate: the precipitate caused by caustic potassa is blue or green; that formed by the carbonate is bright red; and that by the ferrocyanuret of potassium is of a greenish grey colour. Ammonia and the carbonate of this base redissolve the precipitates at first formed. Zinc does not precipitate metallic cobalt from solutions of these salts.

17. *Salts of Nickel.* These have a green or greenish yellow colour; a sweet and astringent taste. The ferrocyanuret of potassium precipitates them of a bright greenish yellow colour; the hydrosulphates precipitate them black; sulphureted hydrogen does not precipitate the solutions formed

by strong acids. According to Tupputi, nickel is not precipitated by any other metal; zinc, however, precipitates part of it in the state of green hydrated oxide. Oxide of nickel forms double salts with all the ammoniacal salts; and all the salts of nickel that are insoluble in water, dissolve in ammonia and in the carbonate of that base.

18. *Salts of Zinc.* These have a metallic and very disagreeable astringent taste; they are colourless, and soluble in a sufficient quantity of ammonia: the carbonates precipitate them with disengagement of carbonic acid, the hydrosulphates with disengagement of sulphureted hydrogen; and in both cases the precipitate is white. The infusion of galls does not trouble solutions of these salts.

19. *Salts of Cadmium.* These are generally white and colourless, dissolving almost entirely in water. The solution is not coloured, and has a disagreeable metallic taste. The alkalies, both caustic and in a state of carbonates, as well as the ferrocyanuret of potassium, precipitate them white; sulphureted hydrogen and the hydrosulphates produce orange coloured precipitates; the infusion of galls does not precipitate them. Zinc precipitates metallic cadmium from them; iron does not possess this property.

20. *Salts of Lead.* Lead forms but one series of salts, having the yellow oxide for their base;

those which are soluble have a saccharine astringent taste; they are colourless. The sulphates, and the ferrocyanuret of potassium, precipitate them white; the precipitates formed by sulphureted hydrogen and the hydrosulphates are black. Sulphureted hydrogen is an exceedingly delicate reagent for ascertaining the presence of salts of lead. Tin and zinc precipitate metallic lead from its solutions.

21. *Salts of Tin.*

(*a*) *Salts of the protoxide.* The protoxide of tin has a much greater affinity for acids than the deutoxide; notwithstanding which, the protosalts oxidize easily and pass to the state of persalts. Lead and zinc precipitate tin from solution, either in the metallic state or in the state of oxide. These salts possess an astringent metallic taste, in the highest degree disagreeable. They are nearly colourless; the ferrocyanuret of potassium precipitates them white *, and the hydrosulphates of a brown chocolate colour. Potassa produces a white precipitate, which is soluble in an excess of this alkali. Mixed with the persalts of many metals, such as of iron, copper, or mercury, they reduce them to protosalts: they precipitate gold from its solutions, in the metallic state; or in the form of a powder known by the name of cassius' purple, when the solutions are dilute.

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* If the solution of tin be at all concentrated, a gelatinous mass is produced on the addition of the ferrocyanuret.—*G. O. R.*

(*b*) *Salts of the peroxide.* These are colourless, and do not display any phenomena consequent on reduction when mixed with salts whose bases are reducible. There are few that crystallise. The ferrocyanuret of potassium precipitates them of a white colour; the precipitates formed by sulphureted hydrogen and the hydrosulphates are yellow. *

22. *Salts of Bismuth.* It is not ascertained whether bismuth forms, with oxygen, more than one salifiable base. The salts of bismuth are colourless; they are precipitated by water. Sulphureted hydrogen produces black precipitates in these salts; those formed by the infusion of galls are orange. Copper and tin precipitate bismuth from its solutions, in the metallic state.

23. *Salts of Uranium.* Uranium forms two classes of salts, viz. the green salts with the protoxide for base, and the yellow with the peroxide.

(*a*) *Salts of the protoxide.* These are little known: their solutions are green; the alkalies precipitate a greenish grey hydrated protoxide, which becomes yellow in the air by passing to the state of peroxide. On heating the liquor that contains the deposit of the hydrated protoxide, it assumes a darker colour, and becomes less soluble in the acids. The carbonate of ammonia produces a precipitate in these salts, which is soluble in an excess of the carbonate.

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* M. Berzelius thinks that the powder of cassius consists of a mixture or combination of protoxide of tin and of gold, at a degree of oxidation inferior to that of peroxide.

(*b*) *Salts of the peroxide.* Their solutions are yellow; some react on turmeric paper, like the alkalies. The precipitates which the alkaline carbonates form in them are dissolved by an excess of the precipitant. On treating them with caustic alkali, the precipitate of peroxide of uranium always retains some alkali, and it is impossible to separate this latter from it. The precipitated alkaline uranates acquire a beautiful orange colour by calcination. Among these salts there are many that dissolve in alcohol and ether; the solution, exposed to solar light, assumes a green colour, and the peroxide is reduced to the state of protoxide. (The ferrocyanuret of potassium produces blood-red precipitates, and the hydrosulphates brown precipitates.)

24. *Salts of Copper.*

(*a*) *Salts of the protoxide.* These are little known. They are almost entirely insoluble in water. When moist, they easily oxidise, and are transformed into persalts with excess of base. When caustic potassa is added to them, they become yellow; ammonia forms colourless solutions with them, which, on contact of air, speedily pass to blue.

(*b*) *Salts of the deutoxide.* These have a green or blue colour; a metallic, acrid, and disagreeable taste; and form beautiful dark blue solutions when treated with an excess of ammonia. The ferrocyanuret of potassium precipitates them of a brownish red colour; sulphureted hydrogen and the hydrosulphates precipitate them brown. They form, with almost all ammoniacal salts, double salts, which are soluble in an excess of ammonia. Copper is precipitated in the metallic state by zinc and iron.*

25. *Salts of Mercury.* The salts of mercury, which are soluble, have a peculiar and very disagreeable metallic taste. The presence of mercury can always be established by heating them to redness with carbonate of soda or potassa, in a tube closed at one end; the mercury sublimes in the metallic state. The oxysalts and the haloide salts are also known by the property they possess of depositing metallic mercury when rubbed on a piece of polished copper.

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* If a common needle be suspended in an acidulated solution of copper, which is so dilute as not to be affected by any of the reagents here mentioned, we have a deposit of metallic copper round the needle after a few hours have elapsed; this test is applicable to all organic mixtures, and is one of the most delicate in chemistry.— *G. O. R.*

(*a*) *Salts of the protoxide.* Treated by alkalies, they give a black precipitate of protoxide.

(*b*) *Salts of the peroxide.* These have a much greater affinity for acids than the preceding; it is on this account that the protoxide of mercury is precipitated by the peroxide from most of its solutions. Their taste is very disagreeable. When treated with the alkalies, they decompose, and assume a citron colour; with the alkaline carbonates, they acquire a rust colour. The ferrocyanuret of potassium does not precipitate them; a small quantity of sulphureted hydrogen first produces a white precipitate in solutions of these salts, or else a dark coloured precipitate, which soon passes to white, and is then only a protosalt; but on increasing the quantity of sulphureted hydrogen, the protosalt passes to the state of black sulphuret.

26. *Salts of Silver.* These are colourless, and have a very disagreeable metallic taste; they give a white precipitate with hydrochloric acid, which the light changes to black, and which, when heated by the blow-pipe on charcoal, becomes reduced. All the preceding metals separate metallic silver from the solutions of these salts. They are all more or less soluble in ammonia. The protosalts of iron and the protosalts of tin also precipitate metallic silver. This reaction of the protosalts of iron is particularly remarkable;

for while these salts, at ordinary temperatures, reduce the salts of silver, to pass to the state of persalts, metallic silver reduces the persalts of iron to protosalts at a boiling heat. It is for this reason that, on boiling silver in a solution of peroxide of iron, it is dissolved, and colours the liquor green; but on cooling, the silver precipitates in the metallic state, and the liquor by degrees reassumes its red colour. The solar light blackens most of the salts of silver; but they do not undergo any alteration in the dark.

27. *Salts of Palladium.* These as yet are little known. Their colour is generally reddish brown, similar to that of a strongly calcined solution of platina. The alkalies and earths precipitate an orange powder (which appears to be a basic salt), and ammonia added in excess assumes a bluish green colour. All the preceding metals, except silver, precipitate palladium from them in the metallic state. The protochloruret of tin gives an emerald green colour to the solutions of palladium; and added in greater quantity, it produces a dark orange deposit. The protosulphate of iron precipitates metallic palladium. Infusion of galls forms a green precipitate, but only when ammonia is added to the solution.

28. *Salts of Rhodium.* These salts are yet but little known.

(*a*) *Salts of the protoxide.* They are distinguished by their dark colour, and by insolubility in water.

(*b*) *Salts of the peroxide.* These are obtained by dissolving the peroxide in the acids. The alkaline carbonates, the chlorides of potassium and of sodium, and the ferrocyanuret of potassium, do not precipitate them. The protochloruret of tin gives them a darker colour, and after some time precipitates the peroxide; the precipitate redissolves in the acids. All the preceeding metals, except palladium and silver, precipitate metallic rhodium from these solutions.

29. *Salts of Iridium.* This metal appears to form red, blue, and colourless salts, according to its degrees of oxidation; none of them have been well studied. The red salts are obtained by treating the combination of the blue oxide and of potassa (iridiate), with an acid, and boiling it with a little nitric acid. The blue salts are prepared without nitric acid; and those which are colourless, by treating the red salts with sulphureted hydrogen, sulphurous acid, infusion, of galls or even the ferrocyanuret of potassium.

30. *Salts of Platina.* These salts are distinguished by the property they possess of not being precipitated by the ferrocyanuret of potassium, and by that of the platina being precipitated by most of the metals, not excepting silver.

(*a*) *Salts of the protoxide.* These are little known; they are generally dark coloured, between brown and green; the alkalies separate the black protoxide, which dissolves but slowly in acids; most of them transform it into peroxide, which dissolves, and into metal, which remains.

(*b*) *Salts of the peroxide.* These have a red or reddish brown colour, which in solutions appears orange. The chloruret (chloride) of potassium, and the chloruret of ammonium (muriate of ammonia), form orange precipitates. They form double salts with most of the alkalies and earths which are undecomposable by an excess of alkali or earth. The protosalts of iron do not precipitate these salts, until a solution of mercury is added, and then the deposit is a combination of mercury and platina. The precipitates which the protochloruret of tin forms in these salts are reddish brown; those produced by the hydrosulphates are brown or black.

31. *Salts of Gold.* According to M. Pelletier, gold does not form oxygenated salts; it produces, on the contrary, haloide and sulphosalts. The chlorurets are best known; they are generally easy to decompose; the vegetable acids precipitate the metallic gold, and the acid is destroyed. The perchloride forms double salts with the chlorurets of potassium or sodium, and produces the cassius' purple with protochloruret of tin.

32. *Salts of Tellurium.* The salts of tellurium are not well known. They are colourless, and have a disagreeable metallic taste. The alkalies form white precipitates, soluble in an excess of alkali. Sulphureted hydrogen precipitates them black; the infusion of galls, yellow; antimony, tin, zinc, copper, and phosphorus, precipitate metallic tellurium from them.

34. *Salts of Antimony.* These have a weak metallic taste, and become turbid when diluted with water; the hydrosulphates form orange precipitates. Iron and zinc precipitate metallic antimony; the ferrocyanuret of potassium does not precipitate them in concentrated solution.

34. *Salts of Molybdenum.* Molybdenum forms three series of oxysalts, into which the protoxide, the peroxide, and the molybdic acid enter as bases.

(*a*) *Salts of the protoxide.* These are black and purple, and generally offer the same variations of colour as the salts of peroxide of manganese. Most of them have a green, brown, or black colour, which is possessed by the solution of the peroxide of manganese in cold hydrochloric acid, before the disengagement of chlorine has commenced. These salts, when dissolved, oxidize with less facility than the persalts, and it is easier to evaporate their solutions than those of the last named. Sometimes they have a dark purple colour, especially when there is an excess of acid present, perfectly analogous to that which the salts of manganese assume under certain circumstances. (The alkalies and the alkaline carbonates precipitate the protoxide, which is insoluble in an excess of these substances; on the contrary, an excess of carbonate of ammonia redissolves it.)

(*b*) *Salts of the peroxide* are red when they contain water of crystallisation, and black in the anhydrous state. Their solutions have an astringent, slightly sour, and then a metallic taste. They are coloured brownish yellow by the infusion of galls, and a light, brownish grey deposit forms. The ferrocyanuret of potassium precipitates them black, and the precipitate is insoluble in an excess of this substance. On dipping zinc into them, they become black, and finally yield a black deposit of protoxide, containing zinc. The insoluble salts of the peroxide of molybdenum, when put into an alkaline solution, quickly disappear, as the oxide passes to the state of acid, which dissolves.

(*c*) *Salts having the molybdic acid for base.* In the state in which molybdic acid is found when it deposits from its solution in nitric acid, it dissolves easily in other acids, although it does not possess this property after being calcined to redness or fused. These combinations can also be called double acids, for they act as such with the alkalies; but generally they so much resemble metallic salts, that it would not be presumed that they had an acid for their base.

35. *Salts of Chromium.* Chromium forms two oxides which are both salifiable bases; the salts of the protoxide alone have been examined. They are green and have a sweet astringent taste. The alkalies precipitate them of a greenish grey colour, which becomes a beautiful green by calcination; the ferrocyanuret of potassium precipitates them green; the infusion of nut-galls of a brown colour.

THE END.

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